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Analytical Chemistry

BASED ON THE GERMAN TEXT
OF
F. P. TREADWELL

ENLARGED AND REVISED
BY
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of the
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PREFACE

is volume first appeared in 1904 as a translation of the *Kurzes Le_ch der analytischen Chemie* written by an American who was tea_g in Zürich. F. P. Treadwell was born in New Hampshire in 185_ompleted his education in Germany, and then, after working und_unsen and Victor Meyer, was made professor of analytical chemistry Zurich, where he remained until his death in 1918.

As_ title of the book indicates, it was intended primarily for students_d was meant to be brief and concise. After the first edition, the book's revised from time to time without paying attention to the new editio_of the German text. The basis for the introduction of new metho_and the discarding of old ones was the needs of students at the Massac_setts Institute of Technology, where numerous tests of the method_ave been made.

The l_ature of analytical chemistry has increased greatly during recent y_s, and at present more than one thousand papers are reviewed annually _ *Chemical Abstracts*. Instruments such as the microscope, spectrosc_e, polariscope, refractometer, potentiometer, colorimeter, nephelom_er, and polarograph have come into common use, especially in the bus_laboratories of large industrial plants. In clinical laboratories, too_advances in chemical technique have made it possible to determine v_y small quantities of important elements in a few drops of a body fluid. No one man can hope to be expert in all the fields of chemical endeavo_ and no *short* textbook_can cover all the ground.

In this r_ision, the entire text has been examined critically and, though many_hanges have been made, the size of the book remains the same. It is s_ll an inexpensive textbook which is meant to be useful to students of ch_mistry and to serve those who desire precise information concerning we_known analytical methods.

The book h_s been divided into chapters, and the methods of gravimetric analysis_ave been rearranged to correspond to the order in which the elements a_e detected in the usual scheme of qualitative analysis. A similar chang_ was made in the ninth edition of Volume I.

The theory _f qualitative analysis applies to quantitative methods, and for this rea_on much of the pertinent theory is discussed in Volume I although some _f it is repeated because many readers will not own the companion volume.

The work of revision has covered a period of more than a year. T
manuscript originally submitted to the publisher was so long that
seemed best to go over it again and by deletions and condensations br
the book back to the size of the eighth edition. As much old mater
has been dropped, not without some misgivings, as new material
been introduced. Thus the introduction of a new procedure develo
at the National Bureau of Standards for the determination of six me
of the platinum group meant the rejection of the classic procedu
Deville and Stas, which was certainly of historical interest.

Although care has been taken in preparing the manuscript a n
reading the proof, doubtless some errors will be found. The   er
would welcome criticism from readers with respect to errata or to   ils
in the procedure which could be explained better or changed   the
interest of accuracy. The numerical values have been check and
should correspond to the 1941 table of atomic weights.

WILLIAM T. ALL

February, 1942

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PART I. GRAVIMETRIC ANALYSIS

CHAPTER I

GENERAL CONSIDERATIONS

The purpose of a quantitative analysis is to determine the relative quantity of one or more constituents of a compound or of a mixture. The methods to be employed depend somewhat upon the nature of the substances analyzed so that, as a rule, a qualitative analysis should precede the quantitative one, or, at least, there should be some knowledge of what elements are likely to be present. The chemical reactions used in quantitative analysis are, for the most part, reactions which are used or can be used as qualitative tests, and the chemical principles involved are the same. In quantitative analysis, however, it is necessary to measure accurately the quantity of sample taken and either the quantity of reagent required to cause a definite reaction to take place or the quantity of one of the products formed by the reaction. Quantitative analysis, therefore, differs from qualitative analysis with respect to the necessity of making careful measurements of materials. Since all chemical research is based upon quantitative analysis, it is clear that the ability to make accurate analyses is one of the most important assets of the chemist irrespective of the field in which he may choose to work eventually.

The most important tool of the chemist is the balance by which weighings are made.[1] The balance used by the chemist combines the physical principles of the lever and the pendulum (Fig. 1).[2] The *beam*, from which the *scale pans* are suspended, represents a horizontal lever with two arms of equal length. To be serviceable, a balance must be *accurate* and *sensitive*. It fulfills the first condition if (1) the arms are actually of equal length, (2) the point of support (the fulcrum about which the beam rotates) lies above the center of gravity, and (3) the fulcrum (center

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[1] Strictly speaking, the balance determines masses and not weights. The unit of *mass* is the *gram* and the unit of *weight* is the *dyne* in the absolute system. The mass in grams, multiplied by the acceleration of a falling body due to gravity, gives the weight in dynes. At any given place, therefore, the weights are proportional to the masses, so that it is common practice to neglect the value of gravity and speak of a *weight* of so many grams. The masses determined by the chemical balance are independent of the value of gravity whereas a spring balance may not show the same weights for the same masses at different places on the earth's surface.

[2] Reproduced, by permission, from Catalog 8 of Christian Becker, Inc.

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knife-edge) and the knife-edges from which the pans are suspended lie in the same plane and are parallel to one another.

The beam of the balance is provided with a long pointer which swings over a fixed scale near the base of the balance case. A small adjustable nut on the pointer, sometimes above and sometimes below the beam, serves to raise or lower the center of gravity of the moving parts and thus change the sensitiveness. At one end of the beam, and in some balances at both ends, is found an adjusting screw which serves to make the effective weights of the arms equal.
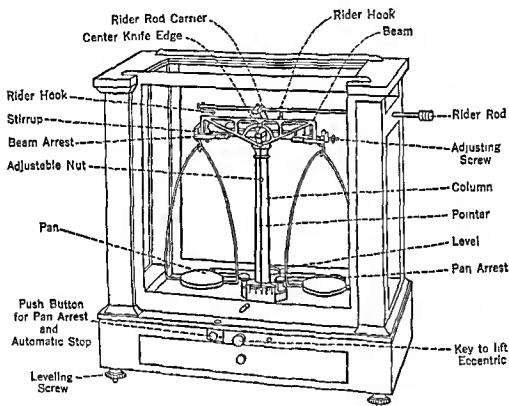
Fig. 1.

At the middle of the beam, on the under side, is a knife-edge which is usually made of polished agate. When the balance is in use, this knife-edge rests upon a plate of polished agate so that the beam can swing with very little friction. At the ends of the beam are other knife-edges from which the balance pans are suspended. When not in use, the beam should be raised so that the knife-edges are not in contact with their bearings. This is effected by means of a frame operated by a key at the front of the balance case. By turning the milled head clockwise, the beam is raised. With an equal load in each pan, and the beam resting on the knife-edge, the pointer should swing an equal number of

divisions both sides of the zero of the scale when the beam is in motion and should finally come to rest at the zero mark. If a small weight is added to either pan the beam and the pointer will swing through an angle and take up a new position of equilibrium. This new position will be the result of the moments of three effective forces — the weight of the beam and the weights in each pan.

The angle α which the pointer at its new resting place makes with its original position is determined by the excess weight, p, the length of the balance arm, l, the weight of the beam, q, and the distance, d, between the center of gravity and the point of support of the beam. Expressed mathematically,

$$\tan \alpha = \frac{p \cdot l}{q \cdot d}$$

The *sensitiveness*, or *sensibility*, is measured by the angle α when p has a definite weight, usually 1 mg. Since the tangent of a small angle is practically the same as the angle, and the tangents of the angles that the pointer makes are directly proportional to the number of divisions between the two points of rest on the scales, it is customary to regard the sensitiveness or sensibility as *the number of scale divisions that the zero point is displaced by an excess weight of 1 mg.*

It follows, then, that the sensitiveness of a balance is directly proportional to the length of the balance arms and inversely proportional to the weight of the beam and to the distance of the center of gravity below the point of support. It is clear also that the observed deflection is proportional to the length of the pointer.

The conditions for maximum sensitiveness are more or less conflicting. Thus long arms are incompatible with minimum weight. The length of arms is also limited by the fact that, the longer the arms are, the greater the time required for one complete swing of the pointer. The weight of the beam also affects the time of swing in the same manner. On the other hand it is important that the beam should be rigid.

Long arm balances, although sensitive, possess the disadvantage of a long time of swing which renders weighing a tedious process. For moderate loads, short arm balances with light beams of aluminum alloy are sensitive and fast.

It is possible to decrease the time of swing by lowering the center of gravity, but this makes the balance less sensitive. For ordinary work, it is well to adjust the sensitiveness so that 1 mg excess weight will displace the zero point about five scale divisions with light loads. The center of gravity must always be below the knife-edge or the balance will be in neutral or unstable equilibrium.

Precautions in the Use of a Balance

1. The balance should rest upon a firm support which is practically free from mechanical vibration. Direct sunlight should not fall upon the balance as it will cause irregularities and errors in weighing.

2. When not in use the balance beam should always be raised off the knife-edges as otherwise these are likely to be injured by jarring.

3. The beam should always be lowered slowly and carefully.

4. The beam should never rest upon the knife-edge while weights or substances are being added to or removed from the pans.

5. The beam may be set swinging by dropping the rider upon the beam or removing it for a moment. It may also be set in motion by fanning one pan gently with a motion of the hand, but in no case should motion be started by touching the pan or by suddenly lowering the beam upon its knife-edge.

6. All weighings should be made methodically, with the weights tried one after another in their proper order.

7. Before making a weight, the adjustment should always be tested. The balance is properly adjusted (a) when it is level, (b) when the pointer rests at the zero mark with the beam raised, (c) the pointer swings equal distances on either side of the zero when the beam is set in motion with no load in the pans.[1] If the balance has pan arrests which work independently of the mechanism that lowers the beam, these arrests should be adjusted so that the pointer is at the zero mark when the beam is on its knife-edge and the pan arrests are in place.

8. Final adjustment with the rider and all observations regarding the swing of the pointer should be made with the balance case closed to prevent errors arising from air currents. When the balance is left, the case should always be closed.

9. The weight of a substance should be recorded, *first*, by adding up the weights missing from the box (in which every weight should always have its own place), and *second*, by adding up the weights that are on the pan. After the final weight has been made, it is convenient to make this second addition when the weights are being returned to the box. By always checking the weights as a matter of habit, serious errors are often avoided.

10. Substances to be analyzed should never be placed directly upon the balance pan but on a watch glass or in a tube. The object should not be warmer or colder than the air in the balance case. Air currents

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[1] Some workers prefer to adjust the balance so that the pointer rests three or four divisions to the right with no load in either pan. Cf. Brinton, *J. Am. Chem. Soc.*, **41**, 1151 (1919).

from a hot body make it weigh too little, and condensation of moisture on a cold body makes it appear too heavy.

11. Care should be taken not to overload the balance.

A separate set of weights should be provided with each balance. In analyzing a given material, the chemist is required to determine the weight ratios of the various constituents. He reports the percentage of iron present rather than the weight. It is important, therefore, that the weights in any set should stand in the proper relation to one another and relatively unimportant whether the 10-g corresponds exactly to the 10-g in some other set. In analyzing ores for precious metals, it is customary to weigh out a large sample on a " pulp balance " which need not be sensitive to 1 mg. The analysis is finished by weighing a very small fragment of metal on a " button balance " sensitive to $\frac{1}{100}$ mg. Ordinarily, however, all the weighings used in any chemical analysis should be made with the same balance and the same set of weights. If a weight is lost or misplaced, a new weight should always be tested to see if it bears the proper relation to the other pieces in the set.

Sets of weights used in chemical analysis usually contain a 50-g weight and sometimes a 100-g weight. Sometimes the smallest weight is 1 mg, but a set need not contain any weight smaller than 5 mg. The numbers on the weights indicate grams when the value is 1 g or over and milligrams if the weight is a fraction of a gram.

Weights smaller than 10 mg are usually obtained by the use of a " rider " or small piece of aluminum wire which may be shifted to various positions on the beam of the balance. The manner in which the beam is divided varies with different makes of balances. When the rider is placed directly over the knife-edge that supports the right pan, it indicates its true weight; and when it is placed at a fraction of the distance between middle and outer knife-edges, it indicates that fraction of its true weight. Riders as a rule weigh 5, 6, 10, or 12 mg. Balances which are made so that the rider can be placed directly over the pan suspension usually take a 10-mg rider or a 5-mg rider. Balances which are made with the top of the beam rounded off at the ends usually take a 12- or 6-mg rider. The larger divisions on the beam graduations are always 1 mg apart when the proper rider is used. The smaller subdivisions are either tenths or fifths of a milligram.

The *chainomatic balance* does not require a separate rider. One end of a small gold chain is fastened to the balance beam and the other end to a hook which can be moved up and down a vertical scale. This hook is operated by a milled bead outside the balance case on the right. Movement of the hook changes the weight of chain that is supported by

the beam so that the positions on the scale correspond to milligrams. This may be adjusted while the balance is in motion.

The magnetically damped balance is useful for rapid and accurate weighings. It is equipped with an aluminum vane suspended from the beam and hung between the poles of a fixed magnet. As the beam swings, induced currents are set up and a magnetic field produced which opposes the motion of the swing so that the beam is quickly brought to rest.

In air-damped balances, large hollow cylinders, closed at the bottom, are fixed just below each stirrup which holds the pans. Inside these cylinders are smaller cylinders suspended from the stirrups. As the balance moves, the smaller cylinders move, and the displacement of the air causes the damping.

Methods of Weighing

It is important to keep the pans, beam, bearings, and all parts of the case clean and free from dust and chemicals. Before starting to weigh, see that the balance is properly adjusted, and determine the *zero point* and the *sensibility* or *sensitiveness*. If necessary, turn the leveling screws at the base of the case until the spirit level back of the pillar shows the correct position. Note also whether the knife-edges are in the proper positions with respect to the bearings and whether the pointer rests at the zero point of the scale. Lower the beam rest, by slowly turning the knurled knob at the bottom of the case in an anti-clockwise direction,[1] and see that the pointer is still at the zero point when the pans are resting on the pan rests, making the proper adjustments, if necessary. Then with the balance case closed, release the pan rests and see that the pointer is quiet or moves back and forth to equal distances on both sides of the zero mark. If necessary, move the adjustment screw on the end of the beam, but it is better to allow for a slight zero error, when it is not more than one scale division, than to make frequent adjustments.

The pointer swings as a pendulum and, owing to air resistance, is subject to a damping, or shortening of the swing, and unless the eye is exactly in alignment, there is a parallax error in reading the position of the pointer on the scale. The halfway point is best determined by taking the halfway point of two or more complete swings. A complete swing of a pendulum involves a return to the starting place, and the measurements will represent complete swings if the final reading is

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[1] In putting anything on the balance pan or taking anything off, the balance beam should always be supported and not resting on the central knife-edge.

taken on the same side as the initial reading so that there will be one more reading on one side than the other (see *Weighing by Swings*). If the center knife-edge is sharp so that there is little friction to overcome save that of the air, the damping will be slight, and negligible if the swing is made short; therefore for ordinary work it is sufficient to take the halfway point of a halfswing, with each turning point less than five scale divisions from the zero mark. With these short swings, moreover, there is less danger of parallax errors than with long swings.

After taking the zero reading, the next thing is to determine the sensibility or *number of scale divisions that the zero point is displaced by a load of 1 mg.* The sensibility varies with the load,[1] but it is well to know how sensitive the balance is at the start because this knowledge will help the operator to make rapid weighings.

Rapid Method. For ordinary work, it is convenient to adjust the center of gravity by means of the adjusting nut on the pointer, so that a load of 1 mg will make the pointer have an initial swing of at least five scale divisions to the left when the pan rests are carefully released. In weighing, note the initial swing when the rider indicates within 0.5 mg of the correct weight. Then change the position of the rider so that the initial swing is a little to the other side of the zero line, and note the new swing; from these two readings estimate where the rider should be to give no swing. This method of making two trials on both sides of the true weight is more rapid and more accurate than attempting to place the rider where the swings will be exactly the same as in making the zero reading. For very precise work, however, weights should be made by the *method of swings*, and corrections should be made for balance-arm error and for buoyancy due to air. The weights should be carefully calibrated.

Single Deflection Method. Adjust the balance so that the pointer swings three or four divisions to the right when the pan support is released and rests on this side of the zero reading on the scale. In weighing, add weights until this same deflection is obtained on releasing the pan support. This method of weighing is rapid but is inapplicable to a balance which has a single release operating both beam and pan supports.[2]

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[1] This is because the center of gravity changes with the load. How this changes, depends upon whether the three bearings lie in the same plane or not. *As a rule, the sensibility is lowered by increasing the load in the balance pans*, partly because the beam becomes slightly distorted and the center of gravity is lowered, but if the three bearings are exactly in the same plane, and the beam is absolutely rigid, the center of gravity will rise, but never reach the level of the middle knife-edge, so that increasing the load will then increase the sensibility.

[2] Brinton, *J. Am. Chem. Soc.*, **41**, 1151 (1919).

Ordinarily, the weight of 1 ml of air at room temperature is assumed to be 1.2 mg,[1] and the density of brass weights is assumed to be 8.4.

If d_1 denotes the density of the *object* weighed, d_2 the density of the weights, ρ the weight of 1 ml of air, p_0 the weight in vacuo, and p the weight in air, the weight in vacuo can be found by the following formula:

$$p_0 = p + \left(\frac{p_0}{d_1} - \frac{p}{d_2}\right)\rho$$

If the density of air is assumed to be 0.0012, which is accurate to only two significant figures, and the density of the substance is given to only two significant figures, not more than three significant figures should be used in the value of p_0 and p in the parenthesis. In the parenthesis, therefore, p_0 can be replaced by p, and we have

$$p_0 = p + \left(\frac{p}{d_1} - \frac{p}{d_2}\right)\rho$$

The use of the above formula can be illustrated by a simple example. If a platinum crucible weighs 15.6954 g in the air with brass weights, what would the crucible weigh in a vacuum? In this case, $p = 15.6954$, $d_2 = 8.4$, and $d_1 = 21.4$. Substituting these values in the formula we have

$$p_0 = 15.6954 + \left(\frac{15.7}{21.4} - \frac{15.7}{8.4}\right)0.0012 = 15.6954 + (0.734 - 1.87)0.0012 = 15.6940$$

It would be a waste of time to try to get the value of the parenthesis with greater accuracy unless the density of the materials is known with greater precision than is assumed here. Note, however, that the value of ρ is usually given in milligrams but is used here in grams.

It may be asked at this point why so much emphasis has been placed upon *brass* weights and why it is assumed that the weights are of brass even although they may be gold-plated or made of platinum. If a set of weights is sent to the Bureau of Standards for calibration and is to be used for very precise work, the Bureau will furnish a certificate which will have two series of corrections. One series will refer to the *apparent mass* as found by comparison with brass standards in air. The other series will make full allowance for the buoyant effect of the air and will refer to the *true mass* of each weight. Since the chemist does his weighing in the air he is interested only in the first set of corrections. With these corrections, the weight obtained in the air is that which would be obtained if the weights were of brass.

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[1] The actual weight in milligrams of 1 ml of air varies with the temperature and pressure as the following table shows.

	16°	20°	22°	24°	26°	28°
730 mm	1 17	1 15	1.14	1.13	1.12	1.11
750 mm	1 20	1.18	1.17	1.16	1.15	1.14
770 mm	1 23	1.21	1 20	1.19	1.19	1.18

(cf. p. 5), start with the 10-mg piece. Let us assume that the balance used is a short-arm Becker balance which takes a 6-mg rider and that the beam reads to about 5.5 mg on the scale.

Place the 5-mg piece whose value is to be tested on the left balance pan and another weight of the same denomination (borrowed from another set) on the right pan. By the method of swings (see p. 8), if an undamped balance is used, determine the rest point, r_1, when the balance is in equilibrium. Now transpose the two weights and determine the rest point r_2 with the weight to be tested on the right balance pan. It is convenient, with a balance in which the beam is graduated only on the right balance arm, to place a small permanent load (a piece of paper or of fine aluminum wire) on the left pan so that all the readings are near the middle of the balance arm. For the calibration assume temporarily that the borrowed weight is correct. In determining the values of r_1 and r_2, carry out the calculations to the nearest 0.05 of a scale division. The sensitivity of the balance should be at least three scale divisions (on the pointer scale) per milligram, and preferably 1 mg = about 5 divisions. From the values r_1 and r_2 the weight of the 5-mg piece tested is

$$5 - \frac{r_2 - r_1}{2S} \quad \text{mg}$$

where S = sensitivity of the balance (see p. 3).

Now take one of the 10-mg pieces, place it on the left balance pan, and weigh it against the two 5-mg pieces. Determine the values of r_1 and r_2 exactly as before. Always start with the pieces already tested on the right pan and the new weight on the left pan; unless the work is done methodically there is danger in getting the sign of the correction wrong. In fact, the commonest error in carrying out a calibration for the first time is to get this sign wrong. One must constantly bear in mind that the piece should have a negative correction if it is too light and a positive correction if it is too heavy. When the piece is too light, r_1 will be smaller than r_2.

Continue testing each weight in the set as follows:

10˙ mg against	"	10
10˙˙	"	10
20 mg	"	10 + 10˙
20˙	"	20
50 mg	"	10 + 10˙ + 10˙˙ + 20 or against 20 + 20˙ + 10
0.1 g	"	0.05 + 0.02 + 0.02˙ + 0.01
0.1˙ g	"	0.1 g
0.2 g	"	0.1 + 0.1˙ g; etc.

CALIBRATION OF WEIGHTS BY TRANSPOSITION

W_1 in Grams	W_2	r_1 in Scale Divisions	r_2 in Scale Divisions	S in Divisions per Milligram	$\dfrac{r_2 - r_1}{2S}$ Milligram	W_3	W_4	Correction in Milligrams
0 005	temporary standard	4 7	..	4 5	..	0 00500	0 00502	−0 02
0 005	5 mg	4 6	4 4	4 5	−0 03	0 00503	0 00502	+0 01
0 010	5 + 5 mg	4 65	4 6	4 5	0 00	0 01003	0 01004	+0 01
0 020	10 + 5 + 5 mg	4 7	4 55	4 5	−0 01	0 02007	0 02007	0 00
0 020	20 mg	4 3	4 3	4 5	−0 05	0 02012	0 02007	+0 05
0 050	20 + 20 + 10 mg	5 0	4 9	4 0	−0 07	0 05015	0 05018	+0 03
0 100	50 + 20 + 20 + 10 mg	5 05	4 8	4 0	+0 03	0 10034	0 10030	+0 02
0 200	100 + 20 + 20 + 20 + 10 mg	4 3	4 25	4 0	−0 10	0 20081	0 20071	+0 10
0 200	200 mg	4 4	5 2	4 0	+0 11	0 20070	0 20071	+0 10
0 500	200 + 200 + 100 mg	4 6	4 8	4 0	+0 05	0 50180	0 50178	+0 02
1 000	500 + 200 + 200 + 100 mg	3 4	4 4	4 0	+0 08	1 00365	1 00356	+0 09
2 000	1 g + 500 + 200 + 200 + 100 mg	4 4	5 4	4 0	+0 19	2 00711	2 00712	+0 01
2 000	2 g	4 45	4 8	4 0	−0 05	2 00706	2 00712	+0 04
5 000	2 + 2 + 1 g	4 4	4 8	4 0	−0 05	5 01785	5 01781	−0 00
10 000	5 + 2 + 2 + 1 g	4 3	3 6	4 0	+0 00	10 03582	10 03582	+0 00
20 000	10 + 5 + 2 + 2 + 1 g	3 6	2 2	3 9	−0 05	20 07133	20 07124	+0 14
20 000	20 g	4 7	3 0	3 5	−0 36	20 07124	20 07124	+0 50
50 000	20 + 20 + 10 g	3 45	3 0	2 7	−0 08	50 17892	50 17810	+0 72

Finally, when every piece in the set has been tested, arrange the data as shown in the table on p. 15. Under the heading W_1 is given the denomination of the weight which is first placed in the left balance pan. Under W_2 is given the temporary value of the weight or weights against which the new piece is tested. The values under r_1, r_2, S, and $\frac{r_2 - r_1}{2S}$ are obtained as described on p. 14. The values given under W_3 represent the temporary calibration values, which are based on the assumption that one of the smallest weights is correct, and those under W_4 are based on the assumption that one of the 10-g weights is correct. When this last assumption is made, it is easier to apply the corrections, as will be evident by comparing the final corrections with the values under W_3.

The calibration of weights is often done by weighing by substitution; another set of weights can be used conveniently as tares. Such weighing *by substitution* (p. 10) is a little easier to explain, but the corrections are more precise in the method of double weighing (weighing *by transposition*). Instead of assuming that one of the 10-g pieces is correct, some prefer to make a comparison with a standard weight, certified by the Bureau of Standards, but this is unnecessary.

Prepare a card from the individual corrections to show the corrections which should be applied to the usual combinations from 0.01 to 1.00 g and from 1 g upward, and keep this card in the balance case. In an ordinary gravimetric analysis, record the weights as follows:

	OBSERVED WEIGHT	CORRECTED MILLIGRAM	CORRECTED WEIGHT
Weight crucible + substance........	19 3105	$\begin{Bmatrix} +0.39 \\ -0.01 \end{Bmatrix}$	19.3109
Weight crucible alone.............	16.9916	$\begin{Bmatrix} +.06 \\ +.06 \end{Bmatrix}$	16 9917
Weight of substance.............			2.3192

The upper correction is that of the weights of 1 g and over; the lower is that of the fractional weights.

When weights are tested at the National Bureau of Standards, each weight is called satisfactory if the error is not greater than a certain value which is called the *tolerance*. The following table shows the tolerance of Class S weights which are suitable for use in analytical chemistry and the precision to which the corrections are determined.

For practical purposes it is advisable to use weights of which the errors are not greater than the tolerances shown in this table on page 17. Then, no serious error is introduced in an analysis by using the un-

corrected values. Few of our procedures have greater accuracy than 1 part in 1,000 and the values specified in the table are all more accurate than this except for the two smallest weights. The most satisfactory plan, therefore, is to make the weights correspond to the standard set by the table below. If a weight is a little too large, owing to corrosion, it can be burnished with fine emery cloth or with metal polish.

PRECISION OF CORRECTION AND TOLERANCES OF WEIGHTS
SUITABLE FOR QUANTITATIVE CHEMICAL ANALYSIS

Denomination	Precision	Tolerance	Denomination	Precision	Tolerance
100 g	0 5 mg	0 5 mg	500 mg	0 01 mg	0.05 mg
50	0 1	0 3	200	0 01	0.05
20	0 1	0 2	100	0 01	0 05
10	0 05	0.15	50	0 01	0 03
2	0 05	0 10	10	0.01	0.01
1	0 05	0 10	5	0 01	0 01

A burnished weight should stand at least 10 minutes before a final test is made. If the weight is too small it should be rejected, unless it is a brass weight with a removable top, when a suitable piece of aluminum wire can be placed inside the piece. The use of lead for this purpose is unsatisfactory because lead corrodes too much.

For testing weights to see whether they conform to the above standards, a balance sensitive to 0.05 mg and one set of calibrated weights is necessary. The calibration of weights is too tedious and involves too many calculations to make it a satisfactory experiment for beginners. Moreover, when a beginner calibrates a set of weights he is likely to make errors either in his computations or in applying the corrections. Often he will make a negative correction when it should be positive. Every set of weights should be tested at least once a year.

Weighing Samples of Factor Weights. In a busy laboratory it is often desirable to weigh out samples in such a way that the results of the analyses are known with as little computation as possible. Thus if the iron content of a sample weighing 0.6994 g is determined by weighing ferric oxide, Fe_2O_3, the percentage of iron, Fe, is exactly 100 times the weight of the oxide. If 1 ml of standard hydrochloric acid will neutralize 0.028 g of pure sodium carbonate, then the percentage purity of a sample of sodium carbonate, containing no other substance of basic nature, will be just twice the number of milliliters of acid used in the analysis of samples weighing 1.4 g. In every technical laboratory, therefore, the chemist has to learn to weigh out rapidly samples of specified weights. If the sample is a dry powder, unaffected

hy contact with the air, it can be weighed out on a watch glass. It is convenient to have a pair of counterpoised watch glasses for this purpose, i.e., a pair of watch glasses which weigh so nearly alike that they can he balanced with the aid of the rider. Metal pans weighing almost exactly 10.000 g can now he purchased and are convenient to use instead of watch glasses.

Place on the left halance pan the watch glass which is to hold the substance, and on the right pan place the tare of the watch glass and additional weights amounting to the desired quantity. With the aid of a small spatula, or a palette knife, transfer some of the powder to the watch glass in the left pan, until the pointer swings to the right with the heam lowered slightly so that the pointer can swing hut a little way. Raise the heam, remove a little of the powder, and, with the heam again lowered a little, add more powder by tapping the spatula. By repeating this process once or twice and finally testing with the halance heam altogether lowered, it is possible to get any desired weight within 0.1 or 0.2 mg. In chemical work it is a waste of time to try to make the original weight much more accurate than the rest of the analysis. Thus, in determining the carbon content of a sample of steel with approximately 1 per cent of carbon present, the results of duplicate analyses with equal weight samples would he considered satisfactory if they indicated 1.00 and 1.01 per cent of carhon. In other words, errors arising from lack of homogeneity and inaccuracies in the method of analysis may easily amount to ½₀₀ of the total carbon content. An error of 0.01 g in the weight of a gram sample of the steel would he no greater than the allowable error of the analysis. In weighing out the sample, therefore, if the weight is accurate to the nearest centigram the error is less than that of the remainder of the work. On the other hand, in determining the chlorine content of a sample of salt weighing about 0.25 g it is important to get the weight to the nearest tenth of a milligram hecause the chlorine determination ean be accomplished with an accuracy of 1 part in 1,000 with samples of this size.

Reliability of a Result. In order that the result of any measurement may be of scientific or technical value, it is desirable to have some numerical estimate or measure of its validity. By the *accuracy* of a result should be understood the degree of concordance between it and the true value of the quantity measured. The true value is not usually known, so that it is not always possible to obtain a numerical measure of the absolute accuracy of a measurement or analysis. By the *precision* or *precision measure* of a result is understood the best numerical measure of its reliability after all known sources of error have been eliminated or allowed for.

When any quantity is measured to the full precision of which the instrument or method is capable, it will usually be found that the results of repeated measurements do not agree exactly. Thus in the analysis of pure salt, the chlorine content will not always be found to be exactly 60.66 per cent although we may have reason to believe that this is the correct value.

All that we can hope to obtain from experimental data is the most probable value of the quantity or quantities in question. The mathematical theory which treats of the general problem of the adjustment of errors of observation so that their effect upon the final result is reduced to a minimum is called the *method of least squares*. According to the theory, the most probable values of a series of related observations are those for which the sum of the squares of the errors is a minimum. This is not the place to go into the details of the mathematical proofs of the method of least squares, but it is important that every chemist should keep constantly in mind certain deductions that have been made from such studies.

In a series of observations, all of which possess an equal degree of probability, the most probable value of the quantity is the arithmetical mean. Since the true value of the quantity is not usually known, the error of each determination and of the mean cannot be determined. It is possible, however, to state how far each observation differs from the mean value, and from these differences the *probable deviation* of the mean can be estimated. The *average* deviation of the mean, usually designated as *ad*, is determined by dividing the sum of the deviations from the mean by the number of determinations made. The *ad* may be regarded as a numerical measure of the amount by which a new observation is likely to differ from the mean value, *m*.

Since the mean has a higher degree of probability than any single observation, it should have a smaller deviation from the truth. It can be shown that an arithmetical mean computed from n equally reliable observations is $\sqrt{n}$ times as reliable as any one observation. The probable deviation of the mean is usually denoted as *AD*. According to the statement just made,

$$AD = \frac{ad}{\sqrt{n}}$$

A little study of this expression shows that it does not pay to increase the number of observations beyond a certain limit as the time and labor involved soon become excessive.

It is probable that more than half the time spent on chemical and physical computations is wasted by the retention of more figures than

the precision of the data warrants. The habit should he acquired of rejecting at each stage of the work all figures which have no influence on the final result. In the following rules for computation the term *digit* denotes any one of the ten numerals including the zero, and the term *significant figure* is any digit which denotes or signifies the amount of the quantity in the place in which it stands. Thus a zero may or may not be a significant figure. When it is used merely to locate the decimal point as in the values 1000 and 0.001, the zero is not a significant figure, for the position of the decimal point is determined solely by the unit in which the quantity is expressed. There are two significant figures in the value 2.5 mg even when it is written 0.0025 g. The number of decimal places in a result has in itself no significance in indicating the precision of a measurement. The statement that the results of an analysis agree within 1.2 mg gives no idea of the precision unless the entire value is known. A fractional or percentage precision measure, on the other hand, gives a definite idea of the precision of the measurement as it involves both the value of the quantity and its average deviation.

Rules for Computations

Rule I. In rejecting superfluous figures, increase by 1 the last figure retained if the following figure (that has been rejected) was 5 or over.

Rule II. In all deviation and precision measures retain two, and only two, significant figures.

Rule III. Retain as many figures in a mean result, and in data, as correspond to the second place of significant figures in the deviation or precision measure. According to this rule, two places of unreliable figures are retained in data so that accumulated errors due to rejections in the course of computation will not affect the first place of uncertain figures. Or, looked at from another point of view, the last figure may be regarded as quite unreliable but the next to the last significant figure should not vary by more than *one* or at the most *two* units from the mean.

Rule IV. The sum or difference of two or more quantities cannot be more precise than the quantity having the largest deviation. In adding or subtracting quantities, find the *ad* of each and retain in each quantity as many places as correspond to the second place of significant figures in the quantity with the largest deviation.

Rule V. In multiplication or division, the percentage precision of the product or quotient cannot be greater than the percentage precision of the least precise factor entering into the computation. Hence, determine the percentage precision of the least reliable factor. If this

is about 10 per cent or better, use three significant figures in each factor of the computation and in the final result. If 1 per cent or better, use four significant figures in each factor of the computation and in the final result. If 0.1 per cent or better, retain five significant figures.

For computations involving a precision not greater than about 0.25 per cent use a 10-inch slide rule.

Rule VI. In carrying out the operations of multiplication and division by logarithms, retain as many places in the mantissa of the logarithm of each factor as are properly retained in the factors themselves under Rule V.

In ordinary chemical work the percentage precision of the result is often less than 0.1 per cent. Thus, in the determination of the chlorine content of a sample of pure salt weighing about 0.2 g, check values of 60.60 and 60.72 per cent chlorine would usually be considered satisfactory. This corresponds to a *percentage precision* of 0.12 part in 61.0, or 0.2 per cent. According to the above rules, only *four* figures should be retained in all factors entering into this computation, and four-place logarithms should be used. In the computation, the molecular weight of silver chloride should be taken as 143.3 instead of 143.34. If, on the other hand, a series of determinations all gave values ranging between 60.63 and 60.69 per cent chlorine, one would be justified in keeping *five* significant figures and using five-place logarithms. This would not necessarily mean that the original weight of the salt and the final weight of the precipitate would have to be carried out to five significant figures, because an error of 0.0002 g in about 0.2 g of salt would correspond to only 0.1 per cent of the entire weight. One would be justified, however, in recording the weights to five decimal places, using the method of swings.

For most chemical work, four significant figures are sufficient. In some cases, as in the determination of sulfur in steel, or in the conversion of small volumes of a solution (less than 1 ml) into an equivalent volume of some other solution, only two significant figures should be used.

Filtration and Washing of Precipitates

How large should the filter be, and how many times should the precipitate be washed?

With regard to the second question it is evident that the precipitate should be washed until the soluble, non-volatile impurity is completely removed. It is clear, however, that this point will never be reached because a part of the solution always remains on the filter, but it is not difficult to make the amount of the dissolved substance remaining

so small as to be negligible. When the amount of soluble impurity remaining on the filter is so small that it could not be detected by the balance, the precipitate can be considered to be completely washed.

The aim should be not only to remove the soluble impurity, but also to accomplish this with as little wash water as possible.

No precipitate is absolutely insoluble, so that it is clear that every unnecessary excess of wash water causes harm by removing a fraction of the precipitate, and the greater the excess of the wash water the greater the amount of the precipitate dissolved.

The amount of wash water to be used depends largely upon the nature of the precipitate itself. Amorphous, gelatinous precipitates always require more washing than crystalline, granular ones. As a rule, it may be said that the process of washing must be continued until the substance which is being washed out can no longer be detected in the last filtrate. If the filtrate must be used for another determination, it is obvious that it should not be tested too soon.

Let us assume the filter to hold 10 ml, the solution to drain to the last drop from the paper, the amount of the solution held back by the precipitate and filter to be 1 ml and to contain 0.1 g of the solid substance which is to be removed by washing.

The filter is filled to the upper edge with wash water and allowed to drain to the last drop n times, until not more than $\frac{1}{100}$ mg of the substance to be removed by washing remains.

According to our assumption, 9 ml drains off and 1 ml remains behind; consequently we have:

REMOVED BY THE	THERE REMAINS AFTER THE
1st washing, $0.1 \cdot \frac{9}{10}$ g	1st washing, $0.1 \cdot \frac{1}{10}$ g
2d " $0.1 \cdot \frac{9}{10} \cdot \frac{1}{10}$ g	2d " $0.1 \cdot \frac{1}{10} \cdot \frac{1}{10}$ g
3d " $0.1 \cdot \frac{9}{10} \cdot (\frac{1}{10})^2$ g	3d " $0.1 \cdot \frac{1}{10} \cdot (\frac{1}{10})^2$ g
.	.
.	.
.	.
nth " $0.1 \cdot \frac{9}{10} \cdot (\frac{1}{10})^{n-1}$ g	nth " $0.1 \cdot \frac{1}{10} \cdot (\frac{1}{10})^{n-1}$ g

After n washings, therefore, the amount removed by washing is the sum of the decreasing geometric series of which the first term is $0.1 \cdot \frac{9}{10}$ and the constant factor is $\frac{1}{10}$.

If $n = 4$, the sum of the series is

$$\Sigma = \frac{0.1 \cdot \frac{9}{10}[(\frac{1}{10})^4 - 1]}{\frac{1}{10} - 1} = 0.09999 \text{ g}$$

After four washings of the precipitate, therefore, 0.09999 g of the impurity has been removed. According to the assumption that there

was originally 0.1 g of this substance, there remains in the precipitate only 0.00001 g, or in other words a negligible amount.

Consequently, the filtrate should be tested qualitatively for the substance to be removed only after the precipitate has been washed four times.

Often the washing will be found to have been complete after the fourth washing, but as a rule this will not be so, and in many cases it will be found necessary to repeat the operation for ten to twenty times. In the processes which are described it will usually be stated how far to carry the washing.

Now in order to wash a precipitate with the least possible amount of wash water, it is evident that the size of the filter paper will have an effect. The filter should be made as small as possible, irrespective of whether there is little or much liquid to filter. *The size of the filter used should be regulated entirely by the amount of the precipitate and not at all by the amount of the liquid to be filtered.* The mistake should not be made, however, of using too small a filter. The precipitate should never reach the upper edge of the paper; about 5 mm should remain free, and even then the filter should not be so

Fig. 4.

completely filled as in Fig. 4a. It is better to have the filter filled about as much as is shown in Fig. 4b, where sufficient room is for the wash water.
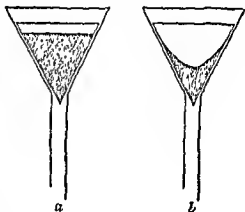
The use of too large filters is one of the inexcusable analytical ——

Purity of Precipitates. In general, precipitation may be ——take place when the *solubility product* (see Vol. 1) is exceeded——fore, by increasing the concentration of the precipitant, ——quantity of other ion, say Cl⁻, required to furnish a ——diminished and the precipitation is more complete. For ——poses, a reaction is complete or *quantitative*, as we often——than 0.1 mg remains in solution. A large excess of ——usually does more harm than good. In many cases ——more soluble in a large excess of reagent. Thus ——soluble in dilute sulfuric acid but after a certain ——the solubility increases and the precipitate di——centrated sulfuric acid. The ——common ——diminish the purity of the :

entrap some of the solution, an *inclusion error;* or some of the soluble ions may stick to the surface of the precipitate, *occlusion or adsorption.*

Colloidal Solutions

When a precipitate forms from a dilute solution, its particles are often very small. In estimating the dimensions of small particles, such as molecules, ions, or finely divided matter in suspension, it is customary to use three linear units: the *micron* = 10^{-6} meter = 10^{-3} mm = 1 μ; the *millimicron* = 10^{-6} mm = 1 mμ; and the *angstrom* (or *Ångström*) = 10^{-7} mm = 0.1 mμ = 1 A. For very small weights the unit γ (gamma) is used, representing 0.001 mg. Some writers have used the symbol $\mu\mu$ for the millimicron, but this practice is likely to lead to confusion; it is better to reserve the letter "m" for one-thousandth and the Greek μ (mu) for one-millionth of a millimeter.

A very large molecule, such as that of starch, when dissolved in water has particles which may be 5 mμ in diameter but the solution shows some of the properties of colloids. In general, molecules in aqueous solution are rarely larger than 1 mμ in diameter, and the ions, although hydrated, are rarely larger than a few angstroms in diameter. If an aqueous solution of an electrolyte is illuminated by a powerful beam of light, there is no scattering of the light rays when the solution is viewed at right angles to the direction of the beam; the solutions are optically "empty" and show nothing when viewed under the ultramicroscope. If particles larger than 100 A (= 10 mμ) are present, they will scatter the light and thus become visible under the ultramicroscope by the so-called *Tyndall effect.*

A solution may appear clear to the naked eye although the particles have much larger than molecular dimensions. Thus, if hydrogen sulfide is passed through a solution of arsenic trioxide, the liquid will become orange in color but it will appear clear if held up before the eye. Under the ultramicroscope myriads of bright particles will be observed in rapid motion, and, if the liquid is placed in a strong beam of light, a marked scattering of the light rays will be noticed. With the ultramicroscope, the presence of particles larger than 10 mμ can be detected. With the ordinary microscope, the limit is about 0.25 μ.

If the particles of a *solute* (substance dissolved) present in a solvent are smaller than 1 mμ we have a *true solution;* if the particles have diameters between 1 mμ and 0.1 μ it is customary to think of the particles as being in *colloidal solution,* and if the particles do not settle out but have diameters larger than 0.1 μ we have what is called a *suspension* although it must be emphasized that this division is arbitrary and there are really no sharp lines between a true solution, a colloidal solution and a suspension.

The physical properties of a true solution (osmotic pressure, lowering of the freezing point, raising of the boiling point, etc.) are determined by the concentration of the solution. A colloidal solution, on the other hand, shows but little depression of the freezing point or rise in boiling point as compared with the pure solvent.

Two types of colloids are formed from aqueous solutions. Some, like silver chloride, show little, if any, attraction for water. Before coagulation their colloidal solutions are only slightly viscous, and when flocculated, the particles settle in a state easy to filter. Such colloids are called *suspensoids* or *hydrophobic* colloids. The colloid held in suspension is called a *sol.* Most of the difficultly soluble inorganic precipitates will yield sols of the above type. The second type of colloid has a marked affinity for water; in the dispersed state (or sol form) such colloids have high viscosity, and when coagulated they settle out in the form of gelatinous solids (*gels*) which

retain large quantities of water in a dispersed condition. This type of colloid is called an *emulsoid* or *hydrophylic colloid*. Silicic acid and hydrated alumina are familiar examples of this type. The distinction between these two kinds of colloids is not an absolute one. In the dispersed state, both types form *sols* or *hydrosols* if the dispersion medium is water. From the hygroscopic gels it is hard to remove all the water, even by strong ignition, but the suspensoids form precipitates which are easy to dry.

It was formerly customary to classify solids as either *crystalline* or *amorphous*, and when this distinction was made it was thought that *true* solutions were obtained from crystalline substances and *colloidal* or pseudo solutions were formed from amorphous solids. This distinction does not seem to be fundamental because many apparently amorphous substances have been found to consist of extremely small crystals and some liquids possess crystalline properties. The size of the particles, as stated above, seems to be the more important criterion. Crystalline solids are characterized by a definite shape of the individual particles. The sides are plane surfaces, and the angles they form with one another are characteristic and always the same for a given crystal. When a beam of X-rays is passed through crystalline material, there is obtained a diffraction pattern of X-rays scattered at various angles from the direction of the beam. From such X-ray studies, it has been shown that the essential feature in a crystal is the arrangement of the atoms, ions, or molecules in a definite pattern which is repeated throughout the crystal. Each positively charged atom is surrounded by a number of negatively charged ones, and conversely for each negatively charged particle. These tiny particles, definitely separated from one another, form what is called the *lattice* of the crystal. The spaces between these particles sometimes permit other material to be entrapped.

Flocculation and Peptization. Colloidal solutions are to be avoided in analytical chemistry because the colloidal particles are so small that they cannot be removed by ordinary filtration. The small particles will remain in a dispersed condition as long as their kinetic motion is sufficient to overcome the gravitational attraction which tends to cause sedimentation. The dispersed particles can be kept in suspension by acquiring an electric charge. This is accomplished by the adsorption of anions or cations on the surface of the particles. Thus radial sulfide sols adsorb sulfide ions, and these are attracted so strongly that they are fixed on the surface of the particles. Whenever such adsorption takes place, there must be adsorption of some

between the negative ions on the surface and the positive *counter ions* (in this case hydrogen ions) are large. A so-called *electrical double layer* is set up between the particles and the solution, the existence of which is responsible for the stability of the sol. All the particles of the sol have the same electric charge and cannot, therefore, approach one another closely. If the double layer is destroyed, as by the addition of a suitable electrolyte, flocculation results. The minimum quantity of electrolyte necessary to flocculate a given colloid is called the *flocculation value*, and it varies with different electrolytes. Thus, to flocculate negatively charged arsenic trisulfide sol, 1000 times as much NH_4Cl is required as $AlCl_3$.

When a colloidal precipitate is washed with pure water, some of the adsorbed ions may be removed, and if the concentration of . . . . the wash water is below the flocculation value, the particles of the . . . . kely to go back to the condition. This is called *peptization;* . . . . . by washing the precip'

with a suitable electrolyte, preferably one which can be subsequently removed by heating.

Sometimes the adsorptive power of a precipitate can be used to advantage; for example, hydrated stannic oxide will adsorb H_3PO_4 and H_3AsO_4 and remove them completely, provided that sufficient colloid is present.

Precipitates formed from very dilute or from very concentrated solutions are in the form of extremely fine crystals with colloidal properties. Thus unfiltrable precipitates of barium sulfate are obtained from solutions which are above 0.75 N in concentration or less than 0 001 N. The precipitates are composed of such tiny crystals that they appear to be amorphous.

Aging of Precipitates. Very fine precipitates often become filtrable if allowed to stand for some time in contact with the mother liquor. Keeping the solution near the boiling point often helps to flocculate a precipitate, and the addition of some macerated filter paper pulp is helpful in filtering colloidal material. The crystals that first form are likely to be imperfect; on standing they tend to perfect themselves. Small particles have a slightly greater solubility than the larger particles; after standing the smaller crystals disappear and the others grow larger. Sometimes the precipitate that forms first is a metastable modification which, on standing, is changed to a more stable and less soluble state.

Coprecipitation. Precipitates are seldom perfectly pure. They may contain a little mother liquor or substances which are normally soluble under the prevailing conditions. Thus, when barium sulfate is formed by adding barium chloride to a solution of potassium sulfate, the precipitate contains a little potassium which is hard to remove by washing, although potassium sulfate is easily dissolved by water. We say that potassium sulfate is *coprecipitated*. This coprecipitation is often caused by adsorption on the surface of the crystal. Adsorption during the growth of a crystal is called *occlusion*; it is different from *inclusion*, which occurs when some mother liquor is entrapped. Sometimes a *solid solution* (also called *mixed crystals*) is formed of two substances which have the same crystalline characteristics. Thus $PbSO_4$ sometimes crystallizes with $BaSO_4$ to form a homogeneous mass or "single phase."

Postprecipitation. Many precipitates are deposited slowly and the solution remains in a state of supersaturation for a long time. Thus, when calcium oxalate is formed in the presence of considerable magnesium ions, the precipitate of $CaC_2O_4 \cdot H_2O$ is practically pure at first, but when it has stood for some time, gradually some of the magnesium is precipitated. Similarly with sulfides, we find that zinc sulfide, for example, is precipitated more readily when a precipitate of HgS or CuS is present. Since, by the precipitation of CuS or HgS from a solution, the acidity of the solution is increased as shown by the equation

$$Cu^{++} + H_2S \rightarrow CuS + 2H^+$$
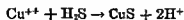
one might expect that ZnS would form more readily from, say, a solution which is 0.1 N in HCl, in the absence of copper ions, although the reverse is true. The coprecipitation of the zinc with copper can be explained by the fact that the copper sulfide precipitate has strong adsorptive powers toward H_2S and, as a result, the concentration of H_2S is greater at the surface of the precipitate than at other parts of the solution.

Equipment and Manipulation

Paper Filters. Strength, uniform texture, proper porosity, and a low ash are the desirable qualities in filter paper for quantitative work. A

paper of 7-cm diameter should have an ash of less than 0.05 mg. To get this low ash, the paper has been washed with hydrochloric and hydrofluoric acids. This washing makes the paper softer and more porous but weakens it so that it is more easily torn.

The purpose of filtration is to separate a solid from the liquid in which it is suspended. The pores of the paper must be smaller than the particles of solid which are to be retained by the filter. Precipitates vary with respect to the size of the smallest particles. Some, like crystalline barium sulfate or gelatinous metastannic acid, are very finely divided and require a fine-grained paper. Such filter paper is a slow filtering medium. Consequently chemists are accustomed to use different grades of filter paper, some which make rapid filters and others which make slow filters but are required for precipitates that are likely to pass through the pores of a rapid filter paper.

Funnels are supposed to have an angle of exactly 60°, and the simplest way to fold a circular cut paper is to crease it across a diameter and then, without opening the paper, make a second fold at right angles to the first one. To test the funnel, and this should always be done before starting to filter, open the filter so that it makes a cone to fit the funnel, wet the paper, and see if it fits tightly against the side walls of the funnel. It is important that it should fit tightly along the upper edge, which must always be below the rim of the funnel as otherwise the filter cannot be washed satisfactorily. Pour water into the funnel, and if the filter fits, the stem should fill with liquid. If the stem is too wide, this will not always happen. A little grease in the stem of the funnel will also interfere. If the filter does not fit when folded into a 60° cone, change the second fold sufficiently to make it fit.

It is convenient to mark the funnel so that it can always be told how much the second fold should be changed to make the filter paper fit the funnel. It is also well to mark the funnel so that it can be recognized as a rapid or as a slow funnel, for funnels vary greatly in this respect.

The above method of folding a filter paper is the easiest and quickest, but often considerable time is saved in the filtration by folding the paper so that liquid passes through it more rapidly. The following method of folding a filter accomplishes this end, but it is harder to make the filter fit tightly to the funnel and there is more danger of having a little precipitate get by the filter.

1. Fold the paper evenly across a diameter of the circle as in the above method.

2. Open up the fold and make another at right angles to it creasing the paper on the same side as at first. This is done by merely bringing the two points on the circumference of the circle that were met by the

first fold over against one another and flattening out the paper again.

3. Turn the paper over and fold again exactly $22\frac{1}{2}°$ away from one of the first two folds. To get this position, bisect one of the quadrants formed by the previous two folds, by merely bringing two creases together and flattening out the paper so that a little crease is made on the circumference, and make another bisection in the same way. At this last mark fold across the paper with the crease on the opposite side to that made by the original folds.

4. Open up the paper and make another fold at right angles to the third fold. Change half of this last fold to make the paper fit the funnel.
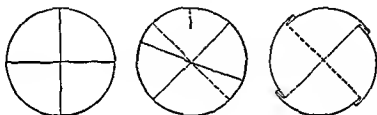
FIG. 5.

Figure 5 shows three stages in folding a filter by the method just described, which has been called *the quadruplet method* because four folds are made instead of the usual two.[1]

For large funnels a *plaited* or *fluted filter* is often desirable. These can be purchased already folded, but the quality of the paper is not always suitable for quantitative work. Swedish filter paper is satisfactory for most purposes when the filter itself is not to be ignited. This can be purchased in sheets, and one-quarter sheet is sufficient for a large funnel. Since all filter paper retains some of the solution poured through it so firmly that it is very difficult to remove the last traces of solute by washing, it is never wise to choose a large funnel simply because considerable liquid has to be filtered. To make a plaited filter:

1. Fold the filter once along a diameter as in the first method. Do not open this fold.

2. Make a second fold along the radius as in the first method.

3. Open this second fold and make two other folds at right angles to each other, dividing the doubled filter into quarters. This is accomplished by taking half of the straight edge of the once-folded filter and folding it over to make it coincide with the second fold. Take care to make all these folds accurately, but do not crease the paper hard at the center.

[1] Mellon, *Methods of Quantitative Analysis.*

4. With the paper again folded only once, make a fold dividing one of the outside segments into halves and make a fold at right angles to this by bringing over the other half of the straight edge.

5. Make two more folds starting with the other outside segment.

By these seven folds the original circle is divided into sixteen parts of equal size, and if the paper is opened, half of the creases will be found all on the same side in one half of the paper and all on the other side in the other half of the paper.

6. With the paper again doubled as it was after the first fold, start at the outside, fold over into the first crease and then bring back the outer edge so that it is in line with the outer edge of the first crease. This makes a subdivision of the outside segment and brings the crease on the opposite side of the doubled paper.

Without opening this last fold, go into the next crease and again come back continuing until the middle fold is reached.

Start in the same way at the other side of the doubled paper and plait toward the center as from the other side.

In this way the paper will be divided into thirty-two equal segments. If the filter is made from a quarter sheet of Swedish paper, it is not necessary to cut out a circle at the start. When the plaiting is finished it is easy to tear off the ends of the folded paper so that it will fit into the funnel, without protruding above the edge, and leave a nearly circular edge.

Plaited filters are used chiefly when it is desired to filter off a large and bulky precipitate and it is not necessary to wash the precipitate thoroughly. Plaited filters made from Swedish paper filter rapidly but are likely to break at the point of the cone.

It is rarely advisable to use suction with a paper filter. The suction is likely to draw small particles of the precipitate into the pores of the paper and then filtration is usually as slow as or slower than it would have been without the suction. If suction is used with a paper filter, the filter should rest in a filtering cone made of platinum, palau, or a hardened parchment filter.

Stirring Rods. Each student should have six or eight stirring rods of suitable lengths. The rod when resting in a beaker should project about 3 cm beyond the lip of the beaker. If small tubing is used, both ends should be sealed; solid rods should be fire-polished at each end. At least one rod should be fitted with a rubber tip (policeman) for removing precipitates which adhere to the walls of beakers. The use of the stirring rod in filtering a solution is shown in Fig. 6. The way the stirring rod is used in transferring a precipitate to a filter by means of a jet of water from a wash bottle is shown in Fig. 7. Note in both

illustrations that the end of the funnel stem is close to the side of the beaker. The funnel should never be allowed to dip into the filtrate, and when it empties into the middle of the beaker there is more or less spattering.
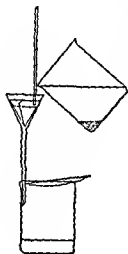
Fig. 6.   Fig. 7.

Filtering Crucibles. The use of a filtering crucible with perforated bottom was first suggested by F. A. Gooch.[1]

A Gooch crucible (Fig. 9) has a perforated bottom. The crucible is provided with an asbestos filter, weighed after drying at the prescribed temperature; then the solution is filtered, with the aid of suction, through the crucible and the precipitate collected in it. After washing the precipitate the crucible and its contents are dried and weighed. The use of this crucible permits rapid and accurate work.

Preparation of Asbestos Filters

Cut some long-fibered, soft asbestos, of the non-hydrated variety, into pieces ½ cm long, and digest with concentrated hydrochloric acid upon the water bath for an hour. A good sample of asbestos will then be separated into very small fibers. Collect the mass in a funnel upon a filter plate, and wash with water until free from chloride. Such washed asbestos can now be purchased from dealers in chemicals.

For the preparation of a Gooch filter, shake some of the material with water in a flask, so that a thin suspension is formed. Stretch a piece of thin rubber tubing (Fig. 8) over a funnel, and place the
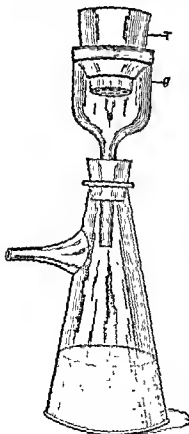
Fig. 8.   Fig. 9.
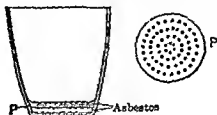
Gooch crucible T in the opening. **The funnel should be large enough so that the crucible is suspended by the rubber without touching the sides of the funnel.** Pour enough asbestos into the crucible to produce a layer of 1- to 2-mm thickness, place a small filter plate (Fig. 9, P), upon this layer, and pour a little more of the asbestos suspension into the crucible. **Wash the felt with water until no asbestos fibers run through, and, in order to see them, pour the liquid into a small beaker.** Usually after a filter is prepared and used with a gentle suction.

If the Gooch crucible and the asbestos are heated to the temperature at which it is desired to heat the precipitate, cooled in a desiccator, and weighed, then the gain in weight after the precipitate has been transferred to the crucible, washed, and heated, represents the weight of the precipitate.

Often it is sufficient to heat the product to a temperature of 105°, for which purpose an automatically controlled electric oven is very serviceable. If it is desired to heat the precipitate to a higher temperature, the Gooch crucible should be heated inside another crucible or in an air bath so that the gas flame does not play directly against the holes in the crucible. Electric ovens are also made which permit drying at temperatures up to 1000°.

A very simple air bath can be made by taking a piece of $\frac{1}{8}$-inch asbestos board, about 4 inches square, and placing a nichrome triangle on it with the ends bent down so that when the crucible is placed in the triangle it will not touch the asbestos. Then, when a burner is placed beneath the asbestos board, the air above the board will be heated and the gas flame will not play directly against the bottom of the crucible.

Sintered-glass filtering crucibles are made of Jena glass and have a porous bottom of sintered ground glass fused to the body of the crucible.

Jena filtering crucibles are obtainable in various degrees of fineness. Each bears a designation etched on the side. Thus a crucible may be marked 1G4. The 1 designates the size and shape of the crucible, the G stands for the kind of glass used (Jenaer Gerateglas), and the number 4 gives the grain size of the fritted glass plate. Of these grain sizes No. 1 has pores averaging 100–120 μ in diameter, No. 2 has pores averaging 40–50 μ, No. 3 has pores of 20–30 μ, and No. 4 has pores of only 5–10 μ (1 μ = 0.001 mm). No. 3 is suitable for moderately fine precipitates, and No. 4 filters so slowly that it should be used only for very fine precipitates like barium sulfate. The highest temperature to which such a crucible can be heated safely is about 600°, and this temperature can be reached without harming the crucible only when the heating and cooling are very gradual. Sintered Jena glass filtering crucibles are very resistant to the action of hot water, dilute acids, and strong ammonia solutions, but they are acted upon by hot solutions containing caustic alkali. Quartz crucibles with sintered bottoms can also be purchased; these can be heated to 1400°.

more hygroscopic. Thus a dried Gooch crucible gained 5.2 mg in weight on standing 24 hours in the air while at the same time a glass filtering crucible gained only 0.3 mg.

For many purposes it is preferable to use instead of a crucible a glass tube with an asbestos filter. This is particularly desirable when it is necessary to heat the precipitate in a gas stream. Filtering tubes can be purchased with sintered glass at the bottom.

These are useful for weighing very small quantities of precipitate in microchemical work.

The so-called Munroe crucible,[1] in which the filtering medium consists of a porous felt of spongy platinum, is a modification of the Gooch crucible which permits rapid and accurate work. The felt is prepared by igniting a carefully dried layer of ammonium chloroplatinate, which has been poured over the bottom of a platinum Gooch crucible in the form of an alcoholic sludge while the crucible is held against several layers of filter paper. The felt can be shaped to the crucible during the ignition and subsequently burnished lightly with a glass rod of suitable form. If imperfections develop, the felt should be saturated again with chloroplatinic acid, the crucible slowly lowered into a moderately concentrated solution of ammonium chloride, washed with alcohol, dried, and ignited. On account of the high price of platinum, the present tendency is to avoid its use as much as possible so that the Munroe crucible has never been popular. The Norton Company of Worchester, Massachusetts, make *Alundum* filtering crucibles which are very rapid but are rather slow to dry to constant weight at low temperatures.
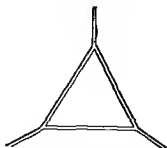
Fig. 10.
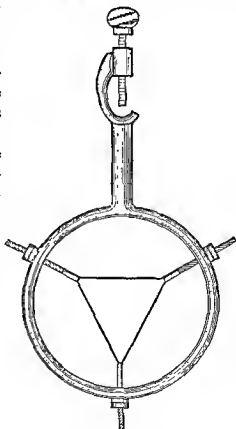
Fig. 11.

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[1] C. E. Munroe, *J. Anal. Chem.*, 2, 241; *Chem. News*, 58, 101. See also W. O. Snelling, *J. Am. Chem. Soc.*, 31, 456, and O. D. Swett, *ibid.*, 31, 928. The last reference gives a table of suitable solvents for removing ignited precipitates from the Munroe crucible.

Triangles. For use with platinum crucibles, platinum triangles are desirable. Figures 10 and 11 represent two forms of these. The first is made of heavy platinum wire and is intended to rest on the ring of a lampstand. The second form is made so that it can be screwed on to the ring and thus kept in place.

Figure 12 shows a clay triangle which can be used even for platinum crucibles, and Fig. 13 represents a less expensive nichrome triangle.
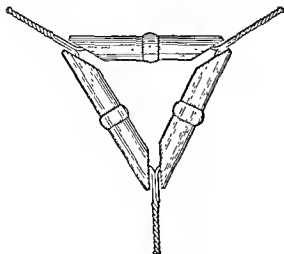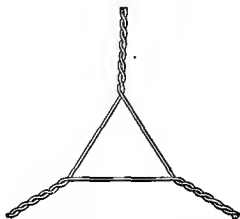
FIG. 12.   FIG. 13.

This may be used with platinum if it is kept clean and no flux is spilled upon it, but there is some danger of staining the crucible with this kind of a triangle.

Triangles of fused quartz are also useful. Figure 14 shows the correct and incorrect ways of placing a crucible on a triangle in an inclined position.
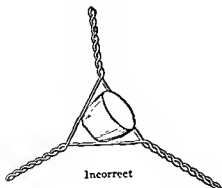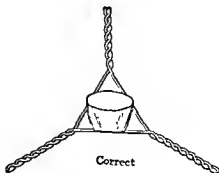
Incorrect   Correct

FIG. 14.

Burners. Besides the ordinary Bunsen burners which are familiar to all, two other types deserve mention. The Tirrill burner is based upon the principle of the Bunsen burner but is an improvement in design. At

the base of the burner the flow of gas is regulated by a screw which operates a needle valve, and the supply of air is regulated by screwing the tube of the burner up or down and thus allowing more or less air to enter through the holes at the base.

The Méker burner provides for a similar adjustment of gas and of air but the shape of the burner tube is different. The tube is narrowest near the base and widens out at the top. As a result the delivery of the gas under pressure into the inverted cone causes a greater reduction of pressure within the tube and a greater inflow of air than in other burners which do not operate with a blast. There is a more perfect mixing of the gas with air and a greater combustion of gas within a given space. At the top of the burner tube is fitted a nickel grid, and the gas burns in a great many small flames with the tip of each inner reducing cone about 1 mm above the top of the burner. The many small flames unite to give a very hot and highly concentrated flame which is oxidizing in character except below the tips of the tiny flame cones. A crucible placed just a little above these tiny flames is heated nearly as hot as by a blast lamp.

Distilled Water. Various forms of stills are in common use. It is important that the vessel containing the boiling water should be so separated from the condenser that there is little danger of spray entering it.

The boiler may be of any material, but the condensing worm and supply pipes should be of pure tin.

Distillation does not free water from carbon dioxide, oxygen, nitrogen, and ammonia, and supply tanks are likely to become slimy after a time. For water analysis and in any work involving the use of water free from nitrogenous compounds, it is necessary to distil the water a second time with permanganate in the boiler. The first and last runnings are then rejected.

Wash Bottles. For transferring a precipitate to a filter and for washing it, a *wash bottle* is indispensable. Figure 15 shows a sketch of the type most commonly used. It consists of a flat-bottomed, 750-ml flask fitted with a rubber stopper and glass tubing bent so that the mouthpiece and outlet tubing are in line. It is best to make the outlet tube in two pieces so that the jet can be manipulated by moving two fingers of the same hand that holds the bottle. The nozzle may be made by

Fig. 15.

drawing out tubing until a capillary is formed and then cutting off to make a stream of the proper size. A stouter tip may be made by simply fusing the end of the original tubing until it has contracted to the proper diameter.

The bend of the long piece of tubing inside the flask is made so that this reaches into the deepest part of liquid when the wash bottle is inclined slightly as in washing precipitates. A bend of the opposite kind is useful for washing precipitates out from beakers, when the bottle is inclined in the opposite direction.

In washing the filter, the stream should always be directed against the upper edge of the paper; this is the hardest part of the paper to wash.

For washing with organic solvents that dissolve rubber, a bottle with a ground-glass stopper is desirable but it is unnecessary for most work in inorganic chemistry.

The wash bottle shown in Fig. 16 is useful for work with hot water or with bad-smelling wash liquids. It contains two tubes like the ordinary wash bottle but at the end of the tube A a Bunsen valve is placed. This is made by cutting a slit in a short piece of rubber tubing, placing this on the end of the tube through which one blows in using the bottle, and sealing the other end of the rubber tubing with a piece of glass rod. On blowing, the slit opens but closes to prevent escape of steam. The third tube C is closed by the finger when using the bottle or by means of rubber tubing and a pinchcock. After blowing through A, a stream of water is ejected at B if C is kept closed. When C is opened the stream stops. It is well to wind the neck of the wash bottle with heavy curtain cord, if it is to be used for hot water.

Policemen. Sometimes a little precipitate adheres to the side of a vessel. To remove it, a piece of rubber over the end of a glass stirring rod is used. This so-called *policeman* may be made by sticking together the end of a piece of rubber tubing that fits the rod tightly, or it may be purchased from a chemical supply house. The policeman should not as a rule be used for stirring a solution and should not be allowed to remain in solutions.

Fig. 16.

Transfer of Liquids. In pouring out a reagent from a bottle never place the stopper on the workbench. Pick up the stopper between the first two fingers of the right hand with the palm up, grasp the bottle with the same hand and the palm over the label, and pour from the bottle with the label up so that there is no danger of any liquid falling upon the label. It is advisable to cover printed labels with thin coatings of gum sandarac dissolved in alcohol. In pouring liquids it is always

advisable to pour against a glass rod so that none of the liquid is spilled. In removing the rod do not move it upward and scrape off a little liquid thereby. It is well to give the rod a slight downward motion on taking it away.

Reagents and Glassware. One of the greatest sources of trouble for the analytical chemist is the presence of impurities in reagents and the action of solutions upon glassware. It is desirable to buy the purest possible reagents, but the chemist should always take care to test them. Even if the reagents are perfectly pure, they often become contaminated by solutions remaining in glass bottles. In every analysis, therefore, errors are likely to arise from impurities that were in the reagents or from glassware that has been somewhat dissolved. Solutions of strong acids and bases when kept for some time in bottles will always give a slight test for silica if sufficient reagent is taken for the test.

Today it is possible to buy glassware which is much less acted upon by reagents than that formerly used. Such glass is essentially a boro-silicate of sodium, zinc, and aluminum.

It is well sometimes to run through blank analyses to see whether any weighable precipitates are obtained when the reagents alone are used in an analysis. Such analyses are often misleading because the precipitates are so small that they may be overlooked or they may be so fine that they need some other precipitate to absorb them and prevent their passage through the filter.

The Evaporation of Liquids. Liquids are usually evaporated upon the water bath. In order to prevent anything from falling into the solution, the beaker or dish should be covered with a watch glass which is raised sufficiently by a glass triangle or a "watch-glass support" to permit escape of the volatilized solvent. Under no circumstances, should the solution be boiled during evaporation as a little of the solution is always carried up with the escaping vapor from a boiling solution.

Evaporation should take place at a temperature below the boiling point of the liquid. If the liquid boils, the escaping gas invariably carries a little entrained liquid with it, and for that reason concentrated solutions should never be allowed to boil. It is safest to evaporate on a steam bath. Vessels that are wide and shallow with rounded bottoms so that they fit well into the holes of the steam bath, the so-called *evaporating dishes* or *basins*, are most suitable. When filled with liquid, they are not very easy to handle, and for that reason many chemists prefer *casseroles* which are provided with handles. Sometimes platinum dishes are desirable, but the high cost and danger of theft prevents their use in many laboratories. Porcelain dishes have been preferred to glass for the evaporation of acid solutions, but it is now possible to buy glass vessels which will resist the action of dilute acids and bases just as well as, if not better than, the better grades of porcelain. Dishes made of fused quartz are light and preferable to either glass or porcelain when they are to be weighed.

Many laboratories prefer hot plates heated either by gas or by electricity to steam baths; for these, the round-bottomed evaporating dishes are not at all suitable because there is very little contact of the bottom with the plate and in moving the dish about there is danger of spilling some of the contents. Unless the heat is controlled so that the evaporating solution does not boil, there is almost always loss by spattering when the solution is evaporated to a small volume on a hot plate. During the evaporation, the dish or beaker should be covered loosely with a watch glass by placing a glass triangle, or glass supports, on the upper edge with a watch glass on top. If the watch glass (or clock glass) is placed directly upon the vessel, the rate of evaporation is retarded; moisture condenses on the under side of the air-cooled watch glass and drops back into the solution. This is particularly serious in evaporating solutions containing sulfuric acid; toward the last the liquid becomes concentrated sulfuric acid and water dropping into it causes very serious spattering.

Flasks are not, as a rule, suitable for evaporations because there is considerable condensation on the sides and neck of the flask. On the other hand, small quantities of solution containing sulfuric acid are evaporated conveniently in Erlenmeyer flasks. If the flask is held by tongs in a somewhat tilted position and is kept in constant motion over a small flame, evaporation is rapid and the sides of the flask serve to prevent loss by spattering. Care must be taken not to let the flame come in contact with any part of the flask that is not being kept wet with the solution or the glass will become overheated and will break when the cooler liquid comes in contact with it. A gentle blast of heated air is sometimes allowed to play upon the surface of an evaporating liquid; this drives away the vapor and hastens the evaporation.

The Drying and Igniting of Precipitates. Before a precipitate can be weighed it is usually necessary to dry it. Those precipitates which do not undergo a change of weight on ignition are treated as follows:

(a) *The Precipitate Is Ignited Dry.* This method, in which the precipitate is separated from the filter, the filter burnt by itself, the ash added to the main part of the precipitate, and the mixture then ignited to constant weight, is used when the ignited substance will be reduced by the burning paper, for example, precipitates of silver chloride, lead sulfate, bismuth oxide, etc.

To perform this operation it is first desirable to dry the filter and precipitate at 100°. Wet a common filter, stretch it over the top of the funnel, and then gently tear off the superfluous paper. The cover thus formed continues to adhere after drying. Place the funnel and filter in a drying-closet and dry at 100–105°. When they are perfectly dry, place a weighed crucible upon a piece of glazed paper of about 20 sq cm (Fig. 18, left) and carefully shake the dry precipitate into the crucible, removing it from the paper as completely as possible by gentle rubbing with a platinum spatula. Brush into the crucible with the aid of a feather any small particles of the precipitate which may have fallen upon the glazed paper (Fig. 18). Small particles of the precipitate will still always adhere to the paper, and these must be weighed. In order

to accomplish this, set fire to the filter and weigh the ash by itself or mixed with the main part of the precipitate.[1]

The combustion of the filter, to which small particles of the precipitate still adhere, is best accomplished by the method proposed by Bunsen as follows: Fold the filter together so that the precipitate occupies the position indicated in the shaded part of Fig. 17 α, and then fold again
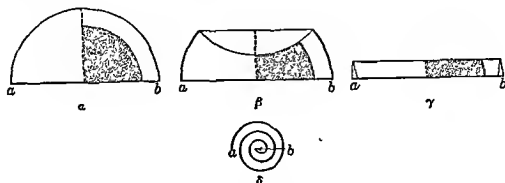
Fig. 17.

as indicated by β and γ of Fig. 17 to a narrow strip. Roll up the paper as indicated by δ, beginning at b, so that the portion of the filter which is free from the precipitate is on the outside. Place the roll in the loop of a platinum wire, hold it over the crucible (see Fig. 18), and set fire to

Fig. 18.

the filter by means of the gas flame. Take away the flame and allow the paper to burn quietly. If carbonized particles still remain, apply the gas flame repeatedly until it is no longer possible to make the particles glow any more. (Too strong ignition should be avoided.) Add the ash to the contents of the crucible by gentle shaking and the final

[1] By using filter paper which has been carefully washed with hydrochloric and hydrofluoric acids, it is permissible to neglect the weight of the ash from the filter itself. With an unknown paper it is necessary to determine the weight of the ash by a separate experiment and then correct the weight of the precipitate obtained.

use of the feather. Heat the crucible at first with a small flame, and gradually raise the temperature until the prescribed temperature of ignition for the given precipitate is reached. Finally remove the flame, allow the crucible to cool somewhat, and while it is still *warm*, but *not glowing*, place it in a desiccator (Fig. 19).

After cooling (at least three-quarters of an hour for porcelain crucibles and 20 minutes for platinum ones) weigh the crucible and its contents.

Many precipitates (silver chloride, lead sulfate, etc.) are partially reduced to metal by the above treatment. As these metals are difficultly volatile, however, there will be no loss of the metal, only of the anion (chlorine in the case of silver chloride and SO_4 in the case of lead sulfate). This loss may be readily replaced. Moisten the metal in the crucible with a few drops of nitric acid to dissolve it, add a few drops of hydrochloric acid (in the case of a silver chloride precipitate), or of sulfuric acid (in the case of lead sulfate), and after evaporating off the excess of the acid, weigh the crucible. The only danger in this method is that in burning the filter the ash is heated too hot, so that some of the reduced metal melts and alloys with the platinum wire. If, however, the filter paper is rolled up as was directed, there is always some paper free from precipitate between the precipitate and the platinum wire, yielding an ash which, although its weight is inappreciable, is still sufficient to protect the wire and prevent the reduced metal from coming in contact with it, provided that it is not heated strongly enough to melt the metal.

Fig. 19.

Many precipitates (K_2PtCl_6, etc.) are changed so much by this treatment that it would be impossible to obtain correct results. With such precipitates the filter cannot be burnt, but it is previously dried at a definite temperature and weighed; afterwards the precipitate and filter are again dried at the same temperature and weighed again.

For drying precipitates an electric oven with automatic temperature control is most advantageous. The regulator can be set at the desired temperature, which will be maintained indefinitely within a few degrees.

(b) *The Precipitate Is Ignited Wet.* Those precipitates which do not suffer any permanent change by the action of the products of combustion of the filter may be ignited wet. Allow the precipitate to drain as much as possible, and while still moist place the filter and precipitate in a crucible, with the paper folded so that the precipitate is not exposed and
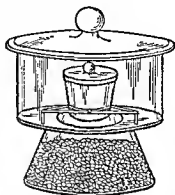
so that the moisture will be expelled through a layer of paper and not directly into the air. Place the crucible in an inclined position upon a triangle (Fig. 20),[1] with the cover inclined against the upper edge of the crucible and resting on the triangle. Direct the flame of the burner against the cover, which quickly dries the filter, then scorches it. Before it takes fire, move the flame to the back of the crucible and heat with a small flame until all the paper is consumed without taking fire, then slowly increase the temperature until finally the crucible is subjected to the whole heat of the burner, after which it can be heated over the blast lamp if necessary.
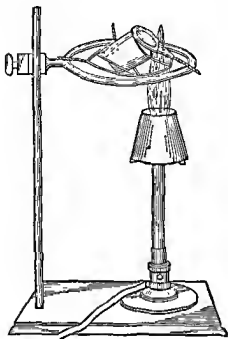
Always in igniting precipitates care should be taken to raise the temperature slowly. The object in keeping the flame near the mouth of the crucible at the start is to make sure that the contents of the crucible are dried from the outside. If the flames were placed at the base of the crucible at the start, there would be more danger of loss by spattering. It is better to use a small flame near the crucible than a large flame with the crucible raised. Care should be taken not to let the paper take fire, except when the bulk of the precipitate has been removed from it and is ignited separately. When the paper burns rapidly in the crucible there is danger of a slight mechanical loss due to the rapid escape of the products of combustion.

Fig. 20.

Too rapid heating of a paper filter may cause two other errors. Often the temperature is raised rapidly enough to fuse a little salt around the ash of the paper, and carbon inside such a fused coating is hard to burn because it is out of contact with the air. This is true, for example, of a silica precipitate, which is likely to retain a little adsorbed alkali salt. If the precipitate is heated rapidly a little carbon is likely to remain even after long ignition over the blast lamp.

Another serious error is sometimes caused by an undesirable reduction. If the filter paper is smoked off slowly at a low temperature it is possible to heat magnesium ammonium phosphate in a platinum crucible with-

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[1] In Fig. 20, the inner triangle is platinum wire, the outer triangle is heavy iron wire. Triangles of fused silica or of nickel-chromium alloy are suitable (cf. p. 33), but platinum alloys with iron, so that a hot crucible should never be placed in contact with iron wire.

out damage to the crucible or to heat ferric hydroxide without getting any magnetite formed.

In the case of magnesium ammonium phosphate it is quite likely that the reduction may be caused by ammonia as well as by carbon. The same principle holds, however, for if the ammonia is expelled slowly at a low temperature there is less danger of a harmful reduction than when the precipitate is decomposed rapidly by strong heating.

When the price of platinum was low, chemists were accustomed to use platinum vessels freely. Thus platinum evaporating dishes, crucibles, filtering cones, spatulas, and heavy platinum wire were used in nearly every chemical laboratory. Since the metal has become more expensive, the chemist is learning how to get along without much of it. Glassware and porcelain are now made of better quality and can be used in chemical work without much contamination. Most ignitions can be made in a porcelain or quartz crucible as well as in platinum. More time is required to cool these crucibles after they have been heated, but the chemist learns to do something else during that time and in the end gets more work done by using a number of porcelain crucibles than he used to do with a few platinum ones.

The Properties and Care of Platinum. Platinum melts at 1770° but does not soften much until this temperature is nearly reached. It resists the action of all common acids except aqua regia and solutions containing chlorine. Long contact with acid ferric chloride solution is also injurious. It forms alloys with easily reducible metals, and platinum crucibles are ruined when such alloys are formed. Long contact with hot carbon injures platinum, some carbide being formed. For this reason a crucible should always be heated with an oxidizing flame; the flame should never show a luminous tip, and the top of the inner cone should be below the bottom of the heated platinum vessel.

Fusion with alkali hydroxides injures platinum, but the metal will stand fusion with alkali carbonate. Compounds of phosphorus are likely to be reduced by hot carbon, and the crucible is ruined when phosphide of platinum is formed.

Iridium has been used to harden platinum but the alloy is less resistant to the action of reagents than pure platinum and the iridium is volatilized appreciably by heating over the blast lamp. Even good platinum ware is likely to become frosted by strong ignition but the surface crystals which cause the frosty appearance should be fine and evenly distributed. A poor platinum alloy will often become covered with a whitish coating and with brown iron oxide stains. In buying platinum it is advisable to get *hammered* rather than *spun* ware, which is more likely to have surface cracks. It is well to specify that no distinct,

uneven discoloration should result from heating, that treatment with acid should show no test for iron after heating 2 hours, that the loss on heating at 1100° should not exceed 0.2 mg per hour over a period of 4 hours, and that 5 per cent of rhodium instead of iridium should be present as hardening agent.

Handle platinum carefully and avoid bending. Use clean tongs for handling hot crucibles, and do not let the tongs come in contact with melted flux.

To clean, use chromic acid for removing organic matter, hydrochloric or nitric acid singly (never mixed) to remove insoluble carbonates or metal oxides. Fuse with sodium carbonate or borax to remove silica or silicates and with alkali pyrosulfate to remove metals or oxides that resist the action of acids.

Never heat platinum with the inner cone of the Bunsen flame touching the vessel; this will cause brittleness.

Do not heat compounds of lead, tin, bismuth, arsenic, antimony, or zinc in platinum. Do not ignite sulfides in platinum, and avoid heating phosphorus compounds except with great care.

Do not attempt to remove fusions with knives, files, glass rods, or other hard tools. Use rubber-tipped rods or solvents.

Polish dull surfaces with sea sand or very fine Carborundum[1] powder.

Preparation of the Substance for Analysis

It is very difficult to give general rules for the preparation of substances for analysis, for it is necessary to proceed differently in different cases. If it is desired to determine the atomic composition of a substance, it is necessary to choose pure material for the analysis. Although this sounds so simple it is often one of the most difficult conditions to fulfill. Many substances are hygroscopic and absorb moisture from the air, which can be removed by heating the substance or by simply allowing it to stand in a desiccator over calcium chloride, provided that the substance itself undergoes no change by this treatment. Many substances containing water of crystallization cannot even be dried in a desiccator, but must be analyzed air-dry. It is always necessary to determine whether the substance to be analyzed possesses a constant weight.

Many commercial salts are prepared pure and can be analyzed directly; usually, however, they have stood for some time in the air and have been handled somewhat, so that they are not so pure as when

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[1] "Carborundum" is the proprietary name of a special make of silicon carbide which is much used as an abrasive.

freshly prepared. Consequently, if it is desired to test the accuracy of an analytical process, the purity of a commercial sample should never be taken for granted. If the substance is soluble in water it can be purified by recrystallization.

Dissolve 10 or 15 g of the commercial salt in the least possible amount of hot water (it is best to use not quite enough water to dissolve the substance *completely*), and pour the hot solution through a plaited filter contained in a funnel with the stem broken off (Fig. 21). This serves to remove all dust or other insoluble impurity. Catch the filtrate in an evaporating dish and cool it rapidly, while stirring constantly, by placing the dish in a larger one containing cold water.

Fig. 21.

By means of the rapid cooling and constant stirring, the salt is obtained in the form of a crystalline powder.[1] Filter off the crystals and drain them by suction. A perforated porcelain plate covered with filter paper may be used in the funnel, or an ordinary filter may be used placed in a perforated filter cone or in a small hardened paper, to prevent tearing the paper by suction. Test the purity of the substance qualitatively by means of some suitable reaction. If it is still not quite pure, repeat the same process of recrystallization until the presence of no impurity can be detected.

Place the pure, moist crystals upon a layer of several thicknesses of clean filter paper, cover with another sheet of filter paper, and allow the crystals to stand for 12 hours at the ordinary temperature. Then weigh out 1 or 2 g of the substance upon a tared watch glass, place it upon a dry glass plate, cover loosely with another watch glass, and allow it to stand for several hours more. If the substance shows no change in

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[1] Large crystals would be obtained by allowing the solution to cool slowly, but they are undesirable, as they usually contain more enclosed mother liquor than the smaller crystals. Most water-soluble salts are much more soluble in hot water than in cold water.

weight it is ready for analysis. Otherwise it must be dried in the air until it no longer shows a change in weight. It is permissible to dry in a desiccator only those substances which will not lose water of crystallization. Deliquescent substances, of course, should not be allowed to remain exposed to the air for very long. Such substances must be quickly dried upon a porous plate and transferred as soon as possible to a flask provided with a closely fitting ground-glass stopper.

For *technical analyses*, the purpose being to determine the cost or selling price of an article or to control its manufacture, the substance must be analyzed *as it is*. The sample should represent as far as possible the average composition of the product.

The selection and preparation of representative samples for analysis are matters of so great importance that they have been discussed in more than 1200 papers[1] written since 1892. The quantity of material from which the sample for analysis should be taken varies with the nature of the material. If it is homogeneous it is merely a matter of grinding a portion until it is of suitable fineness.

The Influence of Fine Grinding on Composition

The rate at which a substance dissolves increases as the amount of surface exposed to the solvent is increased, and for this reason solid substances always dissolve more quickly when reduced to a fine powder. Moreover, when a material undergoes chemical attack, an insoluble substance is often formed and, during the process of solution, the insoluble substance may form a protective coating over particles of material that have not been acted upon. This danger is diminished if the material is in the form of a fine powder. For these reasons the chemist usually prefers to grind a solid substance to an impalpable condition before attempting to analyze it.

This practice, though desirable in most cases and absolutely necessary in others, is accompanied by certain disadvantages. If the material is hard there is always some contamination from the material of which the grinding apparatus is constructed. Thus when the sample is ground in a steel mortar or in a steel ball-mill, it will be contaminated with a little iron, and if ground in an agate mortar with a little silica.[2] Again, if the sample readily undergoes slight decomposition, such a chemical

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[1] Cf. W. J. Sharwood and M. M. Bernewitz, *Bibliography of the Literature on Sampling*, Bureau of Mines Publication. Serial No. 2336.

[2] Hempel (*Z. angew. Chem.*, 1901, 84½) found that an agate mortar and pestle lost 0.052 g in grinding 10 g of glass to a fine powder. E. T. Allen found a loss of 0.145 g of agate in grinding 200 g of quartz.

change is likely to take place during the operation of grinding. In this way the determination of moisture, of ferrous iron, and of sulfur may be influenced very appreciably.

A number of investigators have pointed out the effect of grinding upon the moisture content of a sample. If the sample is practically dry, it is likely to absorb considerable moisture when dried in the air. Thus Hillebrand[1] found that a piece of unglazed porcelain contained no moisture originally, but showed 0.62 per cent of water when ground. If the substance is very hygroscopic, this danger becomes greater. On the other hand, grinding often causes loss of moisture. This is notably true of substances containing water of crystallization or superficial moisture. Thus grinding can easily reduce the moisture content of a sample of gypsum from 20 to 5 per cent, and a sample of coal may show several per cent of moisture when large lumps of it are tested and very little moisture after it is reduced to a fine powder.

The heat produced by grinding may not only serve to expel moisture from the sample, but it may even cause chemical change. Thus Mauzelius[2] has shown, and the experiment has been repeated by Hillebrand[3] that the ferrous iron content of a rock becomes smaller on account of grinding the rock to a fine powder. It has also been found that some sulfur may be lost by long grinding of a sample of pyrite.

The effect of grinding, therefore, accounts for many divergent results obtained by different chemists who have analyzed the same original material.

Sampling a Shipment

To prepare a representative sample from a large mass of material, such as a shipment of ore or of coal, special precautions are necessary. It is never safe to take samples from the top of a large pile of material, but portions should be selected from all parts. The easiest way to do this is in the loading or unloading of the shipment, taking out portions at regular intervals either by a shovel, trowel, or mechanical sampler. In sampling coal, the United States government[4] takes, as a rule, 1000 pounds from each shipment of 500 tons or less. The size to which ore must be crushed for sampling depends on (1) the weight of material given to the chemist from the shipment,[5] (2) the relative value of the rich-

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[1] *The Analysis of Silicate and Carbonate Rock*, Bull. 700, U. S. Geol. Survey.
[2] *Sveriges Geol. Undersökning*, Årsbok 1 (1907).
[3] *J. Am. Chem. Soc.*, 30, 1120 (1908).
[4] G S Pope, *Methods of Sampling Delivered Coal*, Bur. of Mines, Bull 116.
[5] D. W. Brunton, "The Theory and Practice of Ore Sampling," *Trans. Am. Inst. Min. Eng*, 25, 827 (1895).

est mineral value and the average value of the ore, (3) the density of the richest material, and (4) the number of particles of the richest mineral. The more "spotty" the ore the larger must be the original weight selected. The results of Brunton's work show that it is necessary to crush the sample before "cutting it down" and advisable after each "cutting" to crush it still finer.

Crushing the Sample. After enough material has been taken from a shipment to guarantee a representative sample, the next operation is to crush it so that the largest particle is not larger than a certain definite size. Thus, with a sample of coal weighing 1000 pounds, it is all broken up so that the diameter of the largest piece is not more than 1 in. This may be done by a mechanical grinder[1] or by hand with an iron tamping bar or sledge. In mineral analysis, where smaller samples are usually taken, samples are often broken up by pounding on a hardened steel surface with a hardened hammer of the best tool steel.[2]

Mixing and Coning. To mix the sample, it is customary to shovel it into a conical pile. Each shovelful should fall upon the apex of the cone, the material should be thrown so that the cone is not pushed away from its original position, and the shoveler should walk around the cone as he shovels. This serves to bring the finer material near the center of the pile, and the coarser pieces run down the sides. Of the first cone usually one half is rejected. This can be done by shoveling away the cone from the bottom, while walking around the cone, and rejecting every other shovelful. Or the cone may be flattened and quartered.

Quartering. The top of the cone is flattened out and divided into quarters. Opposite quarters are taken for the next crushing.

The mixing, coning, quartering, and crushing should continue until finally a sample of 100–200 g is obtained. When the samples are small enough, the mixing is best done on a sheet of glazed paper, rubber, or oilcloth. A corner of the sheet is lifted and drawn across, low down, in such a way that the material is made to roll over and over and does not merely slide along. The sample should be rolled back and forth along each diagonal for 100 times or more. Then the sample may be spread out into squares and a little taken from each square. In

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[1] W. F. Hillebrand, *The Analysis of Silicate and Carbonate Rocks*, U. S. Geol. Survey, Bull. 700.

[2] Mechanical grinders should be made of specially hardened steel and should be built so that they can be kept clean easily. For laboratory grinding, a modified McKenna ore grinder has been recommended by Hillebrand. (*Bull.* 700, U. S. Geol. Survey.)

weighing out an ore it is always well to mix it by rolling back and forth unless it is extremely fine, when it is not likely to segregate on standing. Segregation takes place when particles are of different sizes and densities.

If, in the sifting of an ore, metallic particles are left on the screen, it is necessary to analyze these particles separately and make a proper allowance in the final calculation. It is necessary then to know the weight of the entire sample and the weight of metal that does not pass through the screen.

In sifting samples, wire screens are commonly used, but inasmuch as a little metal is introduced into the sample, silk bolting cloth is preferable.

The cutting, or dividing, at the several stages of the sampling process is best done by mechanical means. Some machines, of the riffle type, constantly deflect a part of the material that passes through them. Others, which for some purposes are more desirable, change the direction of the fall of the ore at regular intervals. Buckets are constructed so that, as ore is poured into them, half of it is retained and half rejected. Split shovels, consisting of a series of parallel troughs with equally wide spaces between them, are made of various sizes. The ore retained by the shovel, or that which passes through, may be taken for the sample. In using such shovels, of which the smallest size is useful for weighing out samples that are not perfectly homogeneous, allow a thin stream of ore to fall back and forth over the riffle. The distance between riffles should be at least three times the diameter of the largest particles of ore.

In sampling metals and alloys it is necessary to remember that they are seldom homogeneous. During solidification the part that solidifies last is usually different from that which first separates on cooling. As a rule, the outside of an ingot solidifies first and some of the impurities are likely to be concentrated or segregated in the interior. In a steel rail, microscopic examination often shows that the head, the foot, and the web are not exactly the same. The sample used for analysis should consist of borings taken from all over the rail, or, better still, it should be obtained by planing over the entire cross section. A macroscopic[1] survey of the entire cross section after it has been treated with a suitable etching agent, such as an 8 per cent solution of cupric ammonium chloride or a 6 per cent solution of iodine in alcohol for steel specimens, will often show where segregation has taken place. When metals break under strain, the crack usually starts at some place where the material

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[1] Magnifications of less than 10 diameters are often classed as macroscopic, although, strictly speaking, they are not included in an exact definition of the term.

is defective, usually owing to a little enclosed slag. The analysis of the entire material will often fail to indicate a defective material, and the cause of the fracture can be shown only as a result of metallographic examination of polished specimens under the microscope and the chemical analysis of portions where segregation has been revealed by the microscope.

CHAPTER II

GROUPS I AND II OF CATIONS

SILVER, THALLIUM, MERCURY, LEAD, BISMUTH, COPPER, CADMIUM,
ARSENIC, ANTIMONY, TIN, GERMANIUM, MOLYBDENUM, SELENIUM,
TELLURIUM, GOLD, RUTHENIUM, RHODIUM, PALLADIUM, OSMIUM,
IRIDIUM, PLATINUM

All the above cations are precipitated by hydrogen sulfide from solutions which are slightly acidic in mineral acid. Of these 21 elements, 12 are not considered in elementary textbooks on qualitative analysis because of their rarity. For convenience, it is customary to divide the 21 metals into three groups: (1) metals which form sulfides that are insoluble in solutions of alkali sulfides, (2) metals which form sulfides that are soluble in alkali sulfide solutions, and (3) gold and the platinum metals. From the similarity of the metal sulfides of the first subgroup to the metal oxides, this subgroup has been called the *sulfo bases*; and, since the elements of the second subgroup form sulfides comparable with the non-metallic oxides, these elements have been classed as the *sulfo acids*. The platinum metals ruthenium, osmium, rhodium, and palladium can be classed with the sulfo bases, while gold, platinum, and iridium could be considered as belonging with the sulfo acids, but this division of the platinum metals is not a sharp one. Silver, thallium, mercury, and lead are classed as Group I of the usual qualitative scheme; these metals form chlorides which are difficultly soluble in water. The precipitation of lead as chloride is usually incomplete, and insoluble chlorides of mercury and thallium are formed only when these metals are in the univalent state.

(a) METALS WHICH FORM SULFIDES INSOLUBLE IN DILUTE MINERAL ACIDS AND IN SOLUTIONS OF ALKALI SULFIDES

SILVER, THALLIUM, MERCURY, LEAD, BISMUTH, COPPER, AND CADMIUM

SILVER, Ag. At. Wt. 107.88

Forms:[1] AgCl and Ag

Silver occurs native and as the sulfide, telluride, arsenide, antimonide, chloride, bromide, iodide, and in numerous sulfo salts. Native gold usually contains some silver, and the same is often true of native copper. In ordinary mineral analysis, practically all the silver will be precipitated as chloride together with silica, but if any appreciable quantity of silver is present it will be noticeable by the curdy appearance of the precipitate and the fact that it darkens on exposure to light. If ignited together with silica in a platinum crucible, the silver chloride will be reduced to

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[1] Under this heading will be given in every case the symbols of the states in which the element in question is best weighed in gravimetric analysis.

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metal and alloy with the platinum. If silver ions pass into the filtrate from the silica they will not be precipitated unless the solution is saturated with hydrogen sulfide or treated with ammonium sulfide.

Silver is separated from other metal ions as chloride. Lead, palladium, univalent mercury, univalent copper, and univalent thallium are also precipitated as chlorides, and insoluble basic chlorides of antimony or bismuth are often formed by hydrolysis. Silver chloride is not precipitated from alkaline solutions containing alkali cyanide or alkali thiosulfate as silver forms complex soluble cyanide and thiosulfate anions. Interference by organic matter, cyanides, thiosulfates, mercury, copper, and thallium can be prevented by boiling with aqua regia or, except in the case of thallium, nitric acid. Interference of lead can be prevented by prolonged washing of the precipitate with hot, dilute hydrochloric acid or by first precipitating the lead as sulfate. Palladium, which as [PdCl₄]⁼ salt imparts a pink tint to the precipitate of silver chloride, can be removed by repeatedly dissolving the AgCl precipitate in ammonia and reprecipitating it by adding a little nitric acid to neutralize the NH₃.

Determination as Silver Chloride, AgCl

Heat the solution, slightly acid with nitric acid, to boiling and precipitate the silver by the addition of hydrochloric acid, drop by drop, until no more precipitate is formed. Allow the precipitate to settle in a dark place, filter through a Gooch crucible, and wash, first with water containing a little nitric acid until the chloride test can no longer be obtained and then twice with alcohol or water to remove the nitric acid. Dry the precipitate at 100° and finally at 130° till a constant weight is obtained. If it is not desired to use a Gooch crucible for this determination, filter off the silver chloride upon an ordinary washed filter, wash as before, and dry at 100°. Transfer as much of the precipitate as possible to a weighed porcelain crucible, burn the filter (as described on p. 38), and add the ash of the filter to the main portion of the precipitate. Moisten with a little nitric acid and a drop or two of concentrated hydrochloric acid, dry on the water bath, and heat over a low flame until the silver chloride begins to melt. Weigh after cooling in a desiccator.

Solubility of Silver Chloride.[1] One liter of water dissolves 0.00154 g AgCl at 20° and 0.0217 g at 100°. In water containing a *little* hydrochloric acid, the AgCl is less soluble than in pure water, but as the quantity of hydrochloric acid is increased, the solubility of AgCl rises rapidly. Thus 1 l of 1 per cent HCl dissolves only 0.0002 g AgCl at 21°, but 1 l of 5 per cent HCl dissolves 0.0003 g, and 1 l of 10 per cent HCl dissolves 0.0555 g AgCl. By melting the silver chloride there is always loss by volatilization.

Determination as Metal, Ag

Metallic silver is obtained by the ignition of silver oxide, carbonate, cyanide, or the salt of an organic acid. In the last case, the substance

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[1] G. S. Whitby, *Z. anorg. Chem.*, **67**, 108 (1910).

must be heated very cautiously at first in a covered crucible. When the organic substance is completely charred, remove the cover from the crucible and heat until the carbon is completely burned; then weigh the crucible.

From the chloride, bromide (but not the iodide), and sulfide, the metal can be obtained by igniting in a current of hydrogen. The reduction of the chloride, bromide, and iodide can be effected very conveniently by passing the electric current through the substance after it has been melted together. Place the porcelain crucible containing the silver halide in a crystallizing dish and near it place a second crucible containing a little mercury and a small piece of zinc. Upon the silver salt place a small disk of platinum foil, fastened to a platinum wire which dips into the mercury in the other crucible. Fill the crystallizing dish with 1.5 N sulfuric acid so that the crucible is entirely covered with the acid, and allow to stand over night. Next morning all the silver salt will be found to be reduced. Remove the crucible from the acid, wash with water, dry, ignite, and weigh. By this simple method, E. Lagutt obtained excellent results. If the silver halide has not been fused to a compact mass, small particles of the silver precipitate are likely to float around during the operation, and escape reduction.

Separation of Silver from Other Metals

As almost all metal chlorides[1] are soluble in dilute hydrochloric acid, silver is usually separated from the other metals by the addition of hydrochloric acid to the solution. If the solution contains mercurous salts these are oxidized before the addition of the hydrochloric acid by boiling with nitric acid.

For the separation of silver from gold and platinum in alloys see pp. 128, 129, and 132.

Electrolytic Determination of Silver

Silver may be deposited from nitric acid solutions, from ammoniacal solutions, and from potassium cyanide solution.

From nitric acid solution, the electrolysis succeeds under the following conditions: 0.5 g of silver in 150 ml of 0.1 N nitric acid electrolyzed

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[1] The chlorides which may precipitate together with AgCl are Hg_2Cl_2, TlCl, $PbCl_2$, BiOCl and SbOCl. Precipitation of BiOCl and SbOCl is prevented by making the solution more acidic, and these precipitates are soluble in dilute HCl. $PbCl_2$ is easily dissolved by hot water. TlCl is appreciably soluble in hot water but the best way to remove TlCl from a mixture of AgCl and TlCl is to boil the precipitate with aqua regia to convert TlCl to soluble thallic salt, dilute largely and filter off the AgCl.

at 55–60° with the voltage kept between 1.35 and 1.38 volts.   Add 5 ml of alcohol to the bath to prevent the formation of peroxide at the anode. From 6 to 8 hours is required to precipitate the last traces of silver. Wash the electrode without interrupting the current, and dry at 100°.

Determination of Silver in Alloys with Baser Metals by Dry Assay

The cupellation of a silver alloy is carried out in much the same way as will be discussed under the determination of gold.   Use 0.5 g of the alloy, and first determine the approximate silver content by a trial assay. Cupel with 5 g of lead, and weigh the resulting button as described on p. 129.   If the silver is 50 per cent or less, use 8 g of lead for the final assay.   For each per cent of increase in silver content, use 0.1 g less of lead until the content corresponds to 80 per cent silver.   Then decrease the weight of lead more rapidly with increase in the silver content, using 3.5 g of lead for a 90 per cent alloy, 2.3 g of lead for a 93.5 per cent alloy, 1.75 g of lead for a 95 per cent alloy, and only 0.6 g of lead for nearly pure silver.   Unless care is taken to adjust the lead carefully to the silver content, the loss of silver during cupellation is likely to be serious.

For the final assay, cupel 0.5 g of the alloy with the suitable quantity of lead and weigh the button.   Correct for loss of silver by volatilization and absorption by the cupel, by cupelling in the same way and at the same time the corresponding quantities of pure silver and copper. Without this correction, the results are usually 0.4–1.1 per cent too low.

THALLIUM, Tl.   At. Wt. 204.39

Forms: Tl₂CrO₄, Tl₂O₃

The behavior of thallium in mineral analysis depends upon its valence.   If it is in the univalent state and only a little is present, it is likely to escape recognition unless the filtrate from the ammonia precipitation of iron and aluminum is treated with ammonium sulfide before precipitating the calcium; black Tl₂S will be formed. In the trivalent state, thallium is precipitated with ammonia and is likely to be counted as aluminum.   By itself, thallium is not precipitated as sulfide in the presence of mineral acid although the sulfide is insoluble in acetic acid and in solutions of alkali sulfide.   Thallous sulfide is rapidly oxidized by air, soluble thallous sulfate being formed.   Most methods for determining thallium call for its prior reduction to the univalent thallous state which is easily accomplished by adding SO₂ solution in excess and boiling.   The most satisfactory method of weighing thallium is as the chromate, Tl₂CrO₄, but good results can also be obtained by weighing as thallic oxide, Tl₂O₃.   Thallium can also be precipitated as TlI by treating the weakly acidic solution with SO₂ and adding KI in moderate excess.   Under these conditions Cu₂I₂ and AgI are also precipitated

Determination as Thallous Chromate, Tl_2CrO_4 [1]

The solution under examination should contain about 1 mg Tl per ml, no excess quantity of ammonium salt, and nothing that will be precipitated by ammonia, reduce chromic acid, or react with thallium or potassium chromate in the presence of ammonia. Neutralize the acidic solution of thallous salt with ammonia and add 1 ml of strong ammonia in excess for each 100 ml of solution. Heat to about 75° and slowly add, while stirring, a solution of K_2CrO_4 until the solution contains approximately 2 g of K_2CrO_4 in 100 ml. Cool, and filter, after it has stood 12 hours, into a weighed filtering crucible. Wash first with 1 per cent K_2CrO_4 solution and finally with 50 per cent alcohol until all soluble chromate is removed. Dry for an hour at 120–130° and weigh as Tl_2CrO_4.

Determination as Thallic Oxide, Tl_2O_3 [2]

To 50–100 ml of acid solution containing thallium in the univalent state, no reducing agents, no compounds other than thallium that are precipitated by potassium ferricyanide or potassium ferrocyanide in an alkaline solution and no other compounds such as iodide or chromate that will react with thallium, add 5 per cent KOH solution until neutral and 25 ml in excess. Add 25 ml of 8 per cent $K_3Fe(CN)_6 \cdot 3H_2O$ solution and let stand 18 hours. Under these conditions, thallium is oxidized by the ferricyanide to the thallic state and precipitated as hydrated Tl_2O_3. Filter through a weighed filtering crucible, wash with hot water, dry at 200° and weigh as Tl_2O_3.

MERCURY, Hg.   At. Wt. 200.6

Forms: HgS, Hg_2Cl_2, and Hg

Determination as Sulfide

(a) *Precipitation with Hydrogen Sulfide*

The solution should contain not over 0.1 g of mercury as *mercuric* salt in a volume of 100 ml and should contain no oxidizing substances ($FeCl_3$, Cl, much HNO_3, etc.). Saturate with hydrogen sulfide in the cold, allow the precipitate to settle, filter through a filtering crucible, wash with cold water, dry at 105°–110° C, and weigh as HgS.

[1] Browning and Hutchins, *Am. J. Sci.*, [4] 8, 460 (1899); Mach and Lepper, *Z anal Chem.*, 68, 36 (1926); Moses and Brukl, *Monatsh.*, 47, 709 (1926).
[2] Browning and Palmer, *Am J Sci*, [4] 27, 389 (1909); Mach and Lepper, *Z anal Chem*, 68, 41 (1926)

Remark. This method affords excellent results but it is not always applicable, because most solutions to be analyzed contain strong nitric acid (obtained by the solution of impure mercuric sulfide in aqua regia, by the decomposition of organic mercury compounds by the method of Carius, or by the oxidation of mercurous salts). It is not possible to expel the excess of nitric acid by evaporating the solution with hydrochloric acid, because considerable amounts of mercuric chloride are volatilized with the escaping steam. In such a case the following procedure suggested by Volhard should be used:

(b) Precipitation with Ammonium Sulfide

Nearly neutralize the acid solution of the mercuric salt with pure sodium carbonate and treat with a slight excess of freshly prepared ammonium sulfide. Add pure sodium hydroxide solution (free from Ag, Al_2O_3, and SiO_2), while rotating the solution, until the dark liquid begins to lighten; then heat to boiling and add more sodium hydroxide until the liquid is perfectly clear. The solution now contains the mercury as sulfo salt, $Hg\begin{smallmatrix}SNa\\SNa\end{smallmatrix}$. Add ammonium nitrate (5 g for each 100 ml), boil the solution until the ammonia is almost entirely expelled, and allow the precipitate to settle. By means of the boiling with ammonium nitrate, the sulfo salt is decomposed according to the equation:

$$Hg(SNa)_2 + 2NH_4NO_3 = 2NaNO_3 + (NH_4)_2S + HgS$$
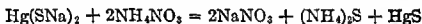
Decant the clear liquid through a Gooch crucible, and wash the precipitate by decantation with hot water until the wash water no longer reacts with silver nitrate solution. Transfer the precipitate to the crucible, dry at 110° C, and weigh. If the precipitate contains free sulfur, boil it with a little sodium sulfite before filtering.[1]

A still better way of removing free sulfur from the precipitate consists of extracting with carbon bisulfide. In this case filter off the mercuric sulfide, together with the sulfur, through a Gooch crucible; wash thoroughly with water and then three times with alcohol. Now place the crucible upon a glass tripod in a beaker containing some carbon bisulfide (Fig. 22).[2] Support the beaker over a vessel filled with hot water and cover it with a round-bottomed flask containing cold water

Cold Water

CS_2

Hot Water
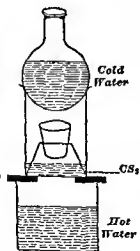
FIG. 22.

[1] By boiling with sodium sulfite, the sulfur is changed to sodium thiosulfate, $Na_2SO_3 + S = Na_2S_2O_3$.

[2] G. Vortmann, Uebungsbeispiele aus der quantitativen chemischen Analyse.

to serve as a condenser. After about an hour the sulfur will be completely extracted. Remove the carbon bisulfide from the precipitate by washing once with alcohol and once with ether. Drive off the ether by gently warming, dry the precipitate at 110° C, and weigh as HgS.

Determination of Mercury in Non-Electrolytes

If it is desired to determine mercury in an organic non-electrolyte, decompose the compound by the method of Carius (see Chapter VI) by heating in a closed tube with concentrated nitric acid, and precipitate the mercury as sulfide by the method of Volhard; or to the acid solution add pure sodium hydroxide solution to alkaline reaction and then enough pure potassium cyanide to dissolve the mercuric oxide. Now saturate the solution with hydrogen sulfide, add ammonium acetate, boil the solution until the ammonia is almost entirely expelled, allow the precipitate to settle, filter, and wash first with hot water, then with hot dilute hydrochloric acid, and finally with water. After drying at 110° C, weigh the precipitate of mercuric sulfide.

Determination as Mercurous Chloride

For the analysis of a solution containing a *mercurous* salt, treat the solution, at a volume of 100 ml for each 0.1 g of mercury, with a slight excess of sodium chloride solution. After it has stood for 12 hours filter through a Gooch crucible, dry at 105° C, and weigh as Hg_2Cl_2. If the solution contains a mercuric salt, first reduce it by the method of H. Rose, using phosphorous acid in the presence of hydrochloric acid as follows:

To the solution of *mercuric* salt (which almost always contains nitric acid) add some hydrochloric acid, enough water to make the volume at least 100 ml for each 0.1 g of mercury, and an excess of phosphorous acid. After 12 hours filter off the precipitate through a Gooch crucible, dry at 105° C, and weigh.

Remark. The results obtained by this method are always about 0 4 per cent too low, but in spite of this fact the method is to be recommended.

The phosphorous acid necessary for this method can be obtained by the oxidation of phosphorus in moist air or by the decomposition of phosphorus trichloride with water, the solution being evaporated to remove the hydrochloric acid and the residue being dissolved in water.

Determination as Metal

Nearly all mercury compounds except the iodide are decomposed quantitatively by heating with lime:

$$2HgX + 2CaO = 2CaX + 2Hg + O_2$$
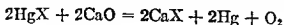
To carry out this determination,[1] take a glass tube 50 cm long and 1.5 cm wide, open at both ends, and near one end place an asbestos plug, follow this with an 8-cm layer of pure lime, then an intimate mixture of a weighed amount of substance with lime, and finally a layer of lime 30 cm long. At the other end of the tube insert another asbestos plug. After the tube has been filled, draw out the tube at the end nearest this second asbestos plug until it is only 4 mm wide. Connect this end of the tube by means of rubber tubing with the empty, narrower arm of a very small Péligot tube. Loosely fill the other and wider end of the Péligot tube with pure gold leaf. Place the glass tube in a combustion furnace and pass illuminating gas (carbon dioxide is less suited) through it for half an hour. Then heat the tube, at first where the 30-cm layer of lime is, then light the other burners one after another until finally the entire contents of the tube are subjected to gentle ignition. During the whole of the operation pass illuminating gas through the apparatus at the rate of about three bubbles a second. The greater part of the mercury collects in the lower empty end of the Péligot tube, and the mercury vapors, which are carried further, amalgamate with the gold. A small amount of the mercury condenses in the drawn-out tube. After cooling the apparatus (in a current of illuminating gas) cut off the narrow part of the tube both sides of the condensed mercury and weigh. Then heat gently, while passing air through the tube to volatilize the mercury, and again weigh. The difference in weight gives the amount of mercury condensed in the combustion tube. The Péligot tube is usually moist; pass dry air through it for some time, and finally weigh it. The gain in weight represents the weight of mercury that amalgamated with the gold.

Although it is easy to obtain good results by this method, it is slower than the sulfide method and is no more accurate.

If it is desired to determine the amount of mercury vapor present in a given space, it is only necessary to aspirate the gas through a calcium chloride tube filled with gold leaf. The gain in weight of the latter shows the amount of mercury present in the gas.

Small quantities of mercury can be detected by reduction with powdered copper followed by amalgamation on gold foil.

To 500 ml of neutral solution in a 750-ml flask add 10–20 ml of concentrated hydrochloric acid and 2 g of powdered copper. Stopper the flask, shake several minutes, and allow to stand over night. Decant off the clear liquid, transfer the copper to an asbestos filter, and wash with water, then with ethyl alcohol and finally with ether. Transfer the air-dried residue to a small, glass bulb tube, taking care to avoid letting any of the copper stick to the sides of the tubing. The transfer can be

[1] First proposed by Erdmann and Marchand, *J. prakt. Chem.*, **31**, 385.

made with the aid of a thin-stemmed funnel. Add a little powdered $MgCO_3$, insert a plug of asbestos at the neck of the bulb, and draw out the tubing about 2 cm above the bulb. Place small pieces of dental gold leaf in the constricted part of the tubing. Heat the bulb uniformly to red heat with wet filter paper on the constricted part of the tubing to keep it cool so that the mercury as it distils from the copper will condense. As little as 0 0001 mg of mercury can be detected.

Small quantities of mercury can be detected electrolytically with a small platinum wire as anode and a fine bright copper wire as a cathode.

Electrolytic Determination of Mercury[1] ,

Mercury can be determined satisfactorily by the electrolysis of acid, neutral, or alkaline solutions. The metal is deposited in the form of little drops, which, when the quantity is small, adhere to the electrode, or, when larger amounts are present, may collect at the bottom of a platinum dish used as cathode.

The electrolysis takes place to advantage in solutions slightly acid with nitric acid.

Procedure. To 150 ml of the neutral or slightly acid solution of the mercurous or mercuric salt in a beaker, add 2 or 3 ml of concentrated nitric acid, and electrolyze with a platinum gauze electrode at room temperature with a current of 0.05–0.10 ampere. The voltage should be between 3.5 and 5 volts. If the electrolysis is started at night, it will be finished next morning, provided that the amount of mercury does not exceed 1 g. By using a current of 0.6–1 ampere the electrolysis is finished at the end of 2 or 3 hours. At the end of the electrolysis, wash the metal with water without interrupting the current, then with alcohol,[2] and dry by touching it with filter paper. Finally keep it in a desiccator over fused potassium hydroxide and a small dish of mercury for several hours. In this way correct results are obtained. Drying at 100° and then over sulfuric acid in a desiccator gives rise to low results because the acid absorbs considerable mercury vapor.

During the electrolysis of mercuric chloride[3] the solution often becomes turbid from the formation of insoluble mercurous chloride; this does no harm, however, as the metal is subsequently deposited on the cathode.

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[1] Luckow, Z anal. Chem , 19, 15 (1880); Smith and Knerr, Am Chem. J , 8, 206; F. W. Clarke, Ber , 11, 1409 (1878); Rüdorff, Z. angew. Chem , 1894, 388; Classen and Ludwig, Ber , 19, 324 (1886); G. Vortmann, Ber., 24, 2750 (1891).

[2] It is usually stated that alcohol is not to be used, but with gauze electrodes it does no harm

[3] In the electrolysis of the chloride, it is better to use a platinum dish with dull, unpolished inner surface (Classen) because then any mercurous chloride will certainly be reduced to metal, which is not always the case with gauze electrodes. When a dish is used as cathode, wash the electrode, without breaking the circuit, by pouring water into it from a wash bottle while the solution is being siphoned off. As soon as the ammeter reaches the zero mark, the washing is finished. Turn off the current, pour off the solution carefully, dry the electrode as above, and weigh.

Mercury can also be electrolyzed from a solution in potassium eyanide in the presence of some caustic alkali, and similarly from a solution formed by dissolving mercuric sulfide in 50–60 ml of concentrated sodium sulfide solution.

The great advantage of the electrolytic determination of mercury lies in the fact that good deposits are obtained irrespective of the nature of the acid radical, or element, which is combined with mercury.

LEAD, Pb. At. Wt. 207.2

Forms: PbO, $PbSO_4$, PbO_2, $PbMoO_4$, $PbCrO_4$, and in rare cases $PbCl_2$[1]

1. Determination as Lead Oxide, PbO

If the lead is present as carbonate, nitrate, or peroxide, it is only necessary to ignite a weighed portion in a porcelain crucible over a small flame and weigh the residue. The treatment of the nitrate requires care, because on rapid ignition the mass decrepitates.

2. Determination as Lead Sulfate, PbSO₄

If the lead is present in solution in the form of its chloride or nitrate, add an excess of dilute sulfuric acid[2] and evaporate the mixture on the water bath as far as possible, then over a free flame until dense white fumes of sulfuric acid are evolved. Cool, dilute with 15 volumes of water, stir, allow to stand some hours, and filter through a Gooch crucible. Wash at first with 8 per cent sulfuric acid (by weight), then with alcohol, and dry at 100°. Place the Gooch crucible in a larger porcelain crucible provided with an asbestos ring, and ignite over the full flame of a Teclu or Tirrill burner or heat the crucible in a muffle to 500–600°. The addition of an equal volume of alcohol before filtering off the $PbSO_4$ precipitate is advisable except when alkaline earth is present.

If it is desired to use an ordinary filter, finally wash the precipitate with alcohol until the wash liquid no longer gives the sulfuric acid reaction, dry, transfer as much of it as possible to a piece of glazed paper, and cover it with a watch glass. Ignite the paper together with some precipitate in a tared porcelain crucible. The hot carbon will reduce some of the $PbSO_4$ to Pb. Moisten with nitric acid and a drop of H_2SO_4, and heat carefully until all excess acid is evolved. Then add the bulk of the precipitate and heat again.

If the lead is originally present as acetate, treat the solution with an excess of

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[1] See analysis of vanadinite.

[2] The solution at the time of filtering should contain about 5 per cent of free sulfuric acid.

dilute sulfuric acid and twice its volume of alcohol, filter after standing some hours, and treat the precipitate of lead sulfate exactly as described above.

To determine the lead present in organic compounds, place the substance in a large porcelain crucible, treat with an excess of concentrated sulfuric acid, and very cautiously heat in the covered crucible over a free flame until the sulfuric acid is completely expelled. Then gently ignite the crucible; if the residue is white, it is ready to be weighed. Otherwise add more sulfuric acid and repeat the process until finally a white residue is obtained.

If the organic lead compound is soluble in water, it is preferable first to precipitate the lead by means of hydrogen sulfide and then transform the precipitate into sulfate. For this purpose, place as much as possible of the washed and dried lead sulfide precipitate upon a watch glass; heat the filter, and remainder of the precipitate in a large porcelain crucible, which is supported in an inclined position. Heat carefully over a small flame until the filter paper is completely consumed. Add the main part of the precipitate to the crucible, cover with a watch glass, and treat with concentrated nitric acid at the temperature of the water bath. When the main reaction is over, repeat the treatment with strong nitric acid until the contents of the crucible are pure white in color. Then remove the watch glass, add 5 or 10 drops of dilute sulfuric acid, and evaporate the liquid as far as possible on the water bath. Remove the excess of sulfuric acid by heating in an air bath which can be made from a larger, metal crucible fitted with a wire triangle to support the smaller crucible; cool and weigh the lead sulfate. Should the precipitate be dark colored after the ignition, moisten it with concentrated sulfuric acid and again expel the excess of acid.

If the lead is present in an organic compound which is not capable of dissociation, the compound should be decomposed in a closed tube with strong nitric acid according to the method of Carius (see Chapter VI), finally washing out the contents of the tube, adding sulfuric acid, and treating the precipitate as described above.

Separation of Lead Sulfate from Barium Sulfate and Silicic Acid

In the analysis of sulfide ores containing lead, it is customary to dissolve the finely powdered ore in nitric acid, or aqua regia, and to remove the volatile acids by evaporation with sulfuric acid, eventually heating over the free flame until fumes of sulfuric acid come off thickly. The sulfuric acid should be diluted with an equal volume of water before being added to the original solution; usually 10 ml of the diluted acid is sufficient. After the evaporation, allow the moist residue to cool, add 100 ml of water, and filter off the precipitate, washing it with 5 per cent sulfuric acid. The precipitate contains all the lead as sulfate but often contains silica and barium sulfate (also strontium sulfate and sometimes calcium sulfate). If only a little impurity is present, treat the precipitate with hot ammonium acetate solution (made by neutralizing 6 N acetic acid with 6 N ammonia, and leaving the mixture barely ammoniacal). When the precipitate is large in amount it is best to wash it into a beaker or flask and heat it with about 20 ml of 2 N ammonium acetate solution (or enough to dissolve all the lead sulfate), then filter through the original filter, and wash with hot ammonium

acetate solution and finally with hot water until the filtrate gives no blackening with ammonium sulfide. Small precipitates of lead sulfate can be dissolved on the filter. The silica and barium sulfate will remain undissolved, but calcium sulfate will follow the lead sulfate.

To obtain lead from the acetate solution, precipitate it as sulfide by hydrogen sulfide, and transform, after drying, into sulfate as described on p. 59. Or add 10 ml of 18 N sulfuric acid to 100 ml of the ammonium acetate solution, remove the acetic acid by evaporation, allow the residue to cool, dilute with water to 100 ml, and filter the lead sulfate into a Gooch crucible. Wash the precipitate with cold 5 per cent sulfuric acid, beat in an air bath, and weigh.

If the amount of ammonium acetate solution used is not too large, the lead may be precipitated by adding enough sulfuric acid to the acetate solution to make the solution contain from 5 to 10 per cent sulfuric acid by weight. Sometimes the precipitate is not pure lead sulfate, in which case it should be redissolved in ammonium acetate and the precipitation as sulfate repeated.

With lead ores containing more substantial amounts of alkaline-earth sulfates, evaporation of the nitric solution of the ore with sulfuric acid gives a residue of sulfates containing a variable amount of lead in the form of a mixed precipitate (Ba, Pb)SO₄, insoluble in ammonium acetate. Such ores should be decomposed with hydrochloric and a little nitric acid, the liquid evaporated to dryness, the residue digested with 20 ml of strong hydrochloric acid, and the acid diluted to 200 ml with hot water. Then, after filtering and thoroughly washing with hot water to dissolve all the lead chloride, the silica and barium sulfate will remain insoluble. Nearly neutralize the filtrate with ammonia and pass H₂S into the slightly acid solution to precipitate PbS, and after extraction of antimony sulfide, etc., if present, with sodium sulfide, dissolve *in HNO₃* and convert into sulfate by evaporating with H₂SO₄, etc., as described on p. 59.

3. Determination as Lead Molybdate, PbMoO₄

In the absence of alkaline earths, chromates, arsenates, or phosphates, the determination of lead as PbMoO₄ is advantageous. The precipitate is less soluble than PbSO₄ and has a high molecular weight. The introduction of molybdate, however, is objectionable if other ions are to be determined in the filtrate from the lead determination.

Procedure. Dilute the solution containing preferably not more than 0.5 g of lead to about 200 ml and add 0.5 ml of 6 N HNO₃. Heat to boiling and slowly add, while stirring, a 2.5 per cent aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O. When the precipitation appears to be com-

plete, let the precipitate settle and add a few more drops of the reagent but avoid a large excess. When the precipitation is complete add 6 N NH₄OH until the solution is faintly basic to litmus paper, then add a few drops of acetic acid. After about 15 minutes, filter through a weighed filtering crucible and wash with hot 2 per cent ammonium nitrate solution. Place in a radiator or muffle and heat slowly to dull redness. Weigh as $PhMoO_4$.

4. Determination as Lead Chromate, $PhCrO_4$

The determination of lead as chromate has been recommended often but since the composition of the heated precipitate does not correspond exactly to the formula $PbCrO_4$ the method is not to be recommended except for determining small quantities of lead. Even then it is advisable to carry out a determination with a known quantity of lead under precisely the same conditions and from this find an empirical factor to be used in calculating the results. A precipitate of $PbSO_4$ which can hardly be seen can be dissolved in hot ammonium acetate solution and will give a much more characteristic yellow lead chromate precipitate

Procedure. Precipitate not more than 0.05 g of lead as sulfate as described under the "Determination of Lead as Sulfate." Wash the precipitate with dilute H_2SO_4 and transfer to a 250-ml flask as much as possible by making a hole in the filter and washing with a stream of hot water from a wash bottle. Dissolve the precipitate in a very little hot 3 N $NH_4C_2H_3O_2$ (prepared by adding 3 N acetic acid to 3 N ammonia until the solution is slightly acid). Moisten the filter with 3–5 ml of the hot ammonium acetate solution and then wash with a little hot water from a wash bottle. Catch the ammonium acetate and the hot water in the flask containing the bulk of the precipitate. Continue treating the filter paper alternately with small portions of hot ammonium acetate solution and hot water until finally the last washing will give no sign of yellow precipitate upon the addition of a few drops of 0.1 N $K_2Cr_2O_7$ solution; if a precipitate of yellow $PhCrO_4$ is obtained, save it and add it to the main solution after it has been treated with $K_2Cr_2O_7$. It should not be necessary to use more than 25 ml of the 3 N ammonium acetate solution. Finally heat the solution in the flask until all the $PbSO_4$ precipitate is dissolved. Dilute to about 150 ml and add to the boiling solution 0.1 N $K_2Cr_2O_7$ solution from a buret. Ten milliliters of the reagent should be sufficient to precipitate all the lead as yellow $PbCrO_4$ and leave the solution slightly orange in color after the precipitate has settled. Filter, wash the precipitate with hot water until the washings are perfectly colorless, dry at 105–110° for an hour, and weigh as $PhCrO_4$.

Carry out the same procedure with a known quantity of lead salt to

find the empirical factor to he used in calculating the weight of Pb or PbO present. One gram of pure $PhCrO_4 = 0.6411$ g Pb or 0.6906 g PbO. In determining the empirical factor the same quantities of sulfuric acid, ammonium acetate, and potassium dichromate should be used as in the analysis itself.

5. Electrolytic Determination of Lead as Peroxide (PbO₂)

Lead can be deposited as metal upon the cathode by the electrolysis of solutions containing the complex oxalate, the acetate, the hydroxide dissolved in caustic alkali, or the phosphate dissolved either in caustic alkali or in phosphoric acid, d 1.7. The deposit is easily oxidized, and there is always danger of some lead peroxide being formed on the anode. No method for the electrolytic determination of lead is as satisfactory as that depending upon the deposition of all the lead, as PbO_2, on the anode by the electrolysis of a nitric acid solution. The concentration of the nitric acid may be such that no copper will be deposited on the cathode, or more dilute nitric acid may be used and the copper determined simultaneously.

The deposition takes place advantageously upon a sand-blasted platinum gauze anode though Classen preferred a platinum dish whose inner surface has been sand-blasted. Chloride, mercury, arsenic, tellurium, selenium, and manganese should be absent.

Procedure. To 100–150 ml of solution containing not more than 0.1 g lead as nitrate, add 10–15 ml of 15 N HNO_3 and electrolyze at room temperature with a current of 0.5 ampere or at 50–60° for an hour. If it is desired to let the electrolysis run over night, a current of 0.5 ampere is sufficient. To test for completeness of deposition, add water to provide fresh electrode surface and note whether any more deposit forms. Without interrupting the current, raise the electrode, or lower the beaker containing the solution, and wash the anode promptly. Dry at 220° and weigh as PbO_2. The PbO_2 dissolves easily in hot dilute nitric acid containing a little oxalic acid or hydrogen peroxide. After the deposition of the lead, the electrolyte can he neutralized with ammonia and made acid with 2 ml of H_2SO_4, and any copper present deposited upon the cathode.

BISMUTH, Bi. At. Wt. 209.0

Forms: $BiPO_4$, $BiOCl$, Bi_2O_3, Bi_2S_3, Bi

1. Determination as Bismuth Phosphate, $BiPO_4$

It is generally agreed that the determination as phosphate is the most satisfactory method that has been proposed for determining bismuth.[1]

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[1] L. Moser, *Die Bestimmungsmethoden des Wismuths*, Stuttgart, 1909. W. R. Schoeller and E. F. Waterhouse, *Analyst*, **45**, 435 (1920).

Treat the cold solution, containing no chloride and not more than 0.5 g of Bi at a volume of not more than 100 ml, with strong ammonia until a slight permanent precipitate is obtained. Dissolve this in 2 ml of 6 N nitric acid. Heat to boiling, and to the boiling solution add, while stirring constantly, 10 per cent diammonium phosphate solution from a buret, using 20 ml for 0.05 g, 30 ml for 0.1 g, 40 ml for 0.2 g, and 60 ml for 0.4–0.5 g of Bi. When the required volume of phosphate has been added, dilute to 400 ml with boiling water and allow to stand 10–15 minutes on a hot plate or water bath. Decant through a weighed Gooch crucible, and wash the precipitate with 3 per cent ammonium nitrate solution containing a few drops of nitric acid per liter. Dry, ignite gently inside another crucible, and weigh as $BiPO_4$.

Determination of Bismuth in Ores

Digest 1 g of the powdered sample with 15 ml of concentrated hydrochloric acid. Add concentrated nitric acid to dissolve any sulfide and evaporate nearly to dryness. Add 10 ml of nitric acid and again evaporate. Take up the residue in 15 ml of strong hydrochloric acid and dilute with water to about 50 ml. Filter off the siliceous residue and wash with normal hydrochloric acid.

If lead is present, add 1–2 g of fine iron wire and heat at the boiling temperature for 10–20 minutes. If lead is absent omit this treatment and precipitate with hydrogen sulfide at once.

Filter off the metallic bismuth and excess iron, wash with hot water, and return to the original beaker. Dissolve in a little hot hydrochloric acid and a few drops of bromine. When all the bismuth has dissolved, boil off the excess bromine and dilute until the solution is about 0.3 N in hydrochloric acid. Saturate this solution with hydrogen sulfide, filter, and wash with very dilute acid containing hydrogen sulfide. Return the sulfide precipitate to the beaker, and treat with hot 2 N sodium hydroxide and hydrogen sulfide, adding some fresh sodium cyanide solution if copper is present. Filter through the same filter, and wash with hot, dilute sodium sulfide solution. Spread the filter against the side of a beaker and rinse off the precipitate of bismuth sulfide. Clean the paper with hot 6 N nitric acid and then discard it. Add more nitric acid to dissolve all the precipitate and evaporate the resulting bismuth nitrate solution until the sulfur has fused to a transparent globule. Do not use bromine at this stage or low results will be obtained. Filter off the sulfur through a small filter and precipitate the bismuth as phosphate by the procedure described above.

2. Determination of Bismuth as Basic Chloride, BiOCl

To the hydrochloric acid solution, which must not contain any phosphoric acid and preferably contains no sulfuric acid, add ammonia until further addition will cause precipitation. Dilute with considerable water, stir, and allow the precipitate to settle. To the clear supernatant solution add more water and repeat this treatment until further dilution causes no more precipitation. If nitric acid was present in the

solution use dilute ammonium chloride solution instead of pure water. Filter, wash with hot water, dry at 105°, and weigh.[1]

3. Determination as Bismuth Oxide, Bi_2O_3

Solid bismuth nitrate or carbonate is readily changed to the oxide by gentle ignition. When bismuth, however, is present *in solution* as the nitrate, it should be first precipitated as the basic carbonate and this changed by ignition to the oxide.

Procedure. Dilute the solution with water (if a turbidity appears it makes no difference) so that not more than 0.1 g of metal is present in 150 ml, add a slight excess of ammonium carbonate solution, heat to boiling, digest on the steam bath for 2 hours, and allow the precipitate to settle. Filter on paper and wash with hot water.

If the precipitate is small, dissolve it in hot 3 N HNO_3 and evaporate the solution to dryness in a weighed crucible or dish. If the precipitate is large, dry the filter and its contents, transfer the greater part of the dried precipitate to a watch glass, and dissolve what remains on the filter paper as just described. After the evaporation to dryness, add the reserved precipitate. Heat gently at first and finally with the full heat of the Bunsen burner under good oxidizing conditions. Cool and weigh as Bi_2O_3.

4. Colorimetric Determination

Less than 0.5 mg Bi is best detected and determined by the yellow or amber color obtained by treatment with KI in dilute nitric acid. Copper, ferric iron, or anything that will react with potassium iodide to liberate iodine should be absent, and colored salts should not be present in quantities sufficient to color the solution. Interference of lead can be prevented by filtering off the PbI_2 that forms, although large quantities of this yellow precipitate are likely to carry down some bismuth.

Procedure. Transfer 20–30 ml of the solution to a Nessler tube, add 4 ml of 6 N HNO_3, 1 ml of saturated SO_2 solution, 5 ml of 30 per cent potassium iodide, and water to make 50 ml. To another Nessler tube add 40 ml of water, the same quantities of nitric acid, sulfur dioxide, and iodide, and sufficient standard bismuth solution to make the colors match. Prepare the standard solution by dissolving 1 g of bismuth in 25 ml of hot, 6 N HNO_3 and diluting the solution to exactly 1 l. After the determination, add starch indicator solution to both tubes to make sure that the colors are not caused by free iodine; if iodine is present the starch will be colored a deep blue.

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[1] Hillebrand and Lundell recommend determining bismuth as BiOCl when less than 5 mg of Bi is present and the following method for more than 5 mg of Bi. Antimony and tin must be absent in both methods.

5. Electrolytic Determination of Bismuth

Brunck[1] obtained accurate results in the electrolysis of solutions containing just enough nitric acid to prevent the formation of insoluble basic salt; the solution should not be more than 0.3 N in HNO_3. Brunck electrolyzed with platinum gauze electrodes connected directly to the poles of a 2-volt storage cell; before the electrolysis was started the solution was heated to boiling. Usually the metal deposited upon the cathode does not adhere well but is spongy even when the electrolyte is stirred.

COPPER, Cu.   At. Wt. 63.57

Forms: CuO, Cu₂S, Cu, Cu₂(CNS)₂

Forms: CuO, Cu_2S, Cu, $Cu_2(CNS)_2$

1. Determination as Copper Oxide, CuO

The copper solution must be free from organic substances and ammonium salts. Heat it to boiling in a porcelain dish and add pure alkali hydroxide solution, drop by drop, until the precipitate becomes dark brown and is permanent, and the solution itself shows an alkaline reaction toward litmus paper. After the precipitate has settled, carefully pour off the upper liquid through a filter and wash the precipitate by decantation with hot water until the wash water no longer shows an alkaline reaction. Transfer the precipitate to the filter and continue washing with hot water. Usually a small amount of copper oxide adheres to the porcelain dish so firmly that it can be removed only by vigorous rubbing with a glass rod covered at the end with a piece of rubber tubing, and finally when the precipitate is removed from the dish some will then remain on the rubber. Consequently it is better to proceed as follows: Remove as much of the precipitate as possible by a stream of water from the wash bottle, then add 2 drops of 6 N acid, and, by inclining the dish and rubbing with the glass rod, moisten with the acid all the precipitate remaining on the dish. Two drops of the acid are sufficient, with correct manipulation, to dissolve all the copper oxide. Prepare a small fresh filter, and holding the dish in an inclined position, so that the liquid remains near its lip, wash the sides once with hot water and heat the contents of the dish (which is continually maintained in this inclined position) to boiling over a small flame; add dilute potassium hydroxide solution drop by drop until the copper is again precipitated. Avoid a large excess of alkali hydroxide on account of its solvent action upon the precipitate.[2] Quickly pour the contents of the dish through the

[1] O. Brunck, *Ber.*, 35, 1871 (1912).
[2] Cf. Vol. I.

small filter and immediately wash the disb once with water. All the copper oxide is now on the filter. Wash the precipitate with hot water, dry botb filters, and transfer most of the precipitate to a porcelain crucible. Ignite the filters in a platinum spiral, and add the ash to tbe contents of the crucible. Cover the crucible, ignite at first gently, and finally with the full heat of the Bunsen burner; weigh as CuO. If the process is carried out carefully, the results obtained are good but as a rule they are a trifle high.

Remark. According to A. Bayer,[1] copper can be determined in the presence of all other metals of the hydrogen sulfide group in the following manner: Add caustic soda solution to the copper solution until all the copper is precipitated as hydroxide and then add enough Rochelle salt (sodium potassium tartrate) to dissolve the precipitate. Heat to boiling in a porcelain dish, and to the boiling solution add 2 ml of 5 per cent hydroxylamine hydrochloride. By boiling 1 minute all the copper (not more than 0.2 g should be present) is precipitated as cuprous oxide.

$$4Cu\begin{smallmatrix}O \cdot CH \cdot CO_2Na \\ \\ O \cdot CH \cdot CO_2K\end{smallmatrix} + 2NH_2OH + H_2O \rightarrow 2Cu_2O + 4KNaC_4H_4O_6 + N_2O$$
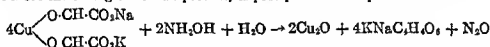
Filter off the cuprous oxide into a Gooch crucible, wash with hot water, dry, ignite in the air, and weigh as CuO.

Usually it is better to precipitate the copper as sulfide, and if the sulfide is heated in the air it is changed to CuO although the older chemists preferred weigh it as Cu₂S after heating with sulfur in an atmosphere of hydrogen (see next method).

Procedure. Adjust the acidity of the solution so that it is about 0.3 N in HCl or H_2SO_4. Heat to boiling, and pass into it a stream of H_2S as the solution is allowed to cool. When cold, stop the flow of the gas, allow the precipitate to settle, and filter through a paper filter. During the filtration, keep the filter well filled with liquid without, of course, letting it rise above the top of the tightly fitting ashless filter. Wash the CuS precipitate with 4 per cent acetic acid solution which has been saturated with H_2S. Finally drain as completely as possible, place paper and precipitate in a weighed porcelain crucible, dry over a small flame, and char the paper without letting it take fire. Then burn off the carbon and raise the temperature to the full heat of the burner while keeping the crucible on its side and with the flame not covering the mouth of the crucible. Cool in a desiccator and weigh as CuO. Repeat the beating and weighing until a constant weight is obtained.

The reason why it is necessary to keep the funnel filled with liquid during the filtration and washing of the cupric sulfide is this: If moist copper sulfide is exposed to the air it is quickly oxidized and the hydrogen sulfide wash water acts upon the salt formed by the oxidation ($CuS_2O_7 \cdot CuSO_4$), and transforms it into colloidal cupric sulfide, which passes through the filter, and on coming in contact with the acid fil-

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[1] *Z. anal. Chem.*, 1912, 729.

trate is coagulated. If, however, the precipitate is not exposed to the air during the filtration there is no oxidation and the filtrate remains clear.

2. Determination as Cuprous Sulfide, Cu₂S

Procedure. Precipitate the copper with H_2S as just described. Dry it by heating in the drying closet at 90–100° for at least an hour.

Transfer as much of the precipitate as possible to a weighed Rose crucible (of unglazed porcelain[1]), burn the filter in a platinum spiral, and allow the ash to fall at first upon an unglazed crucible cover, where it should be heated gently till it glows, in order to make sure that it contains no unburned carbonaceous matter. Then add the ash to the main portion of the precipitate in the crucible. Also add a little sulfur that has been recrystallized from carbon bisulfide. Place the perforated cover on the crucible (Fig. 23), pass a stream of hydrogen through it (the wash bottle shown contains concentrated sulfuric acid[2]), and heat the crucible at first over a small flame and finally so that the bottom of the crucible glows faintly. At this temperature the cupric sulfide is changed to cuprous sulfide,

$$2CuS = Cu_2S + S.$$
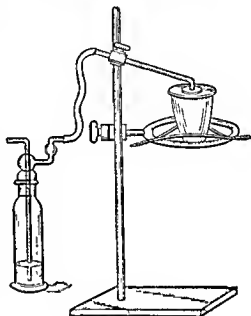
Too strong heating is inadvisable, according to Hampe.[3]

FIG. 23

When the excess of sulfur has been driven off (which can be readily ascertained by removing the cover of the crucible and finding no blue flame and no odor of burning sulfur), increase the current of hydrogen so that eight bubbles per second pass through the wash bottle (at first, not more than four bubbles per second should have been the rate), and remove the flame. Allow the crucible to cool in the current of hydrogen and weigh after it has remained in the desiccator for 15 minutes. The cuprous sulfide should be brownish black or black, and should show no

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[1] A quartz crucible is more desirable, as the transformation of CuS into Cu₂S can then be watched.

[2] If the hydrogen is prepared from zinc and hydrochloric acid, the gas should be passed first through water and then through a wash bottle containing concentrated sulfuric acid.

[3] Z. anal. Chem., 38, 465 (1891).

reddish brown stains (due to Cu or Cu_2O); this is the case if the current of hydrogen was too slow during the cooling. To remedy this defect, add a little sulfur to the precipitate and repeat the heating in hydrogen.

Remark. It is evident that the sulfur used for this experiment should leave on ignition no weighable residue. This is why the sulfur used should be recrystallized from carbon bisulfide.

3. Determination as Cuprous Thiocyanate, $Cu_2(CNS)_2$
Method of Rivot[1]

The solution should be slightly acid with sulfuric or hydrochloric acid and contain 0.2 g or less of copper in 100 ml. Oxidizing agents must be absent. To the solution add an excess of sulfurous acid,[2] and normal ammonium thiocyanate solution, drop by drop with constant stirring, whereby at first a greenish mixture of cupric and cuprous salts is precipitated, which after stirring becomes pure white cuprous thiocyanate. Allow the precipitate to settle completely (this requires several hours). Then filter through a weighed filtering crucible and wash with cold water until the filtrate shows only a slight reddish coloration when ferric chloride is added. Finally wash several times with 20 per cent alcohol, dry at 110–120°, and weigh as $Cu_2(SCN)_2$. The cuprous thiocyanate can be dried at a temperature as high as 160°, but at 180° it begins to decompose. The precipitate permits rapid filtration, and a turbid filtrate is never obtained. After the determination is finished, the greater part of the precipitate can be shaken out of the crucible, and the remainder dissolved in hot nitric acid.

4. Electrolytic Determination of Copper

This most accurate and most convenient of all methods for the determination of copper was first proposed by W. Gibbs in 1864.[3] Copper may be deposited by means of the electric current from acid, alkaline, and neutral solutions, but for analytical purposes an acid solution is commonly used.

Probably no other element is determined so frequently by electrolysis and good deposits can be obtained under widely different conditions. The elements arsenic, antimony, tin, molybdenum, gold, the platinum metals, silver, mercury, bismuth, selenium, and tellurium should all be absent. If lead is present the electrolysis should take place in the presence of nitric acid; if considerable nitric acid is present the lead is deposited first on the anode, and later, after the solution has been somewhat

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[1] Compt. rend., 38, 868; see also R. G. van Name, Z. anorg. Chem., 26, 230, and Busse, Z. anal. Chem., 17, 53, and 30, 122.

[2] Instead of sulfurous acid, ammonium bisulfite may be used, prepared by saturating aqueous ammonia with SO_2.

[3] Z. anal. Chem., 3, 334 (1864).

neutralized or diluted, the copper comes down on the cathode. In dilute nitric acid, the two elements are deposited simultaneously. When copper alone is desired, the best deposits are obtained when the electrolyte contains both nitric and sulfuric acids.

Procedure. To 100–125 ml of solution containing up to 1.0 g of copper in a 150-ml beaker add 2 ml of concentrated sulfuric acid and 1 ml of concentrated nitric acid. Add about 1 g of urea, or more if necessary, to react with any nitrous acid present:

$$2HNO_2 + CO(NH_2)_2 = 2N_2 + CO_2 + 3H_2O$$
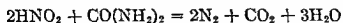
Add the urea until it causes no further evolution of gas. Use preferably cylindrical gauze electrodes with the cathode surrounding the smaller anode and at least 5 mm away from it. The cathode should reach to the bottom of the beaker, but it should not be entirely immersed in the electrolyte. Electrolyze with a current of 1.8–2.0 amperes with the anode rotated during the electrolysis; all the copper should deposit in less than an hour. With an unstirred electrolyte, use a current of 0.2 ampere and continue the electrolysis over night. To make sure that the electrolysis is finished, add a little water, so that a fresh surface of the cathode is wet by the solution, and note whether any fresh deposit of copper is formed. Then, without turning off the current, raise the electrodes, or lower the beaker, while washing the electrodes with a stream of water from a wash bottle. To make sure that all acid is removed, immerse the electrodes in water and then in alcohol. Dry for a minute or two at 105° and weigh. It is easy to tell by watching the electrode when all the alcohol has evaporated. After the electrolysis make the solution ammoniacal and look for a blue coloration. If there is any sign of blue color, and nickel is absent, make the solution slightly acid with sulfuric acid and electrolyze a little longer with a clean cathode.

The results should be within 0.1 per cent of the truth. If nickel is present, test for residual copper by means of water saturated with H_2S. If a slight darkening is obtained in this test, the quantity of copper can usually be estimated colorimetrically or the CuS precipitate can be filtered off, ignited in a porcelain crucible, the ash dissolved in a little HNO_3, and the resulting solution electrolyzed with a clean cathode. During the electrolysis, do not stir the solution fast enough to cause spattering. It is well to wash down the sides of the beaker toward the last. The use of a clean cathode is recommended for determining the last portions of copper when the original deposition was incomplete, because it is then easy to tell whether more copper is being deposited.

CADMIUM, Cd.   At. Wt. 112.4

Forms: Cd, CdSO₄, CdO and Cd₂P₂O₇

1. Electrolytic Determination of Cadmium

Of all the methods for the determination of cadmium the electrolytic method is not only the most convenient, but by far the most accurate, and of the many methods proposed that of Beilstein and Jawein[1] can be recommended. To the solution of the sulfate, add a drop of phenolphthalein indicator solution, and then pure sodium hydroxide solution until a permanent red color is obtained. Now add 10 per cent pure potassium cyanide solution with constant stirring, until the precipitate of cadmium hydroxide produced by the caustic soda has completely dissolved; an excess of potassium cyanide should be scrupulously avoided. Dilute the solution with water to 100–150 ml and electrolyze in the cold, using a gauze cathode. From 5 to 6 hours are required with a current of 0.5–0.7 ampere and an electromotive force of 4.8–5 volts; at the end of this time increase the current to 1–1.2 amperes and electrolyze the solution for 1 hour more. If these directions are followed, all the cadmium (if not more than 0.5 g is present) will be deposited as a firmly adhering, dull deposit of nearly silver-white metal. Stop the current, quickly remove the solution, and wash the deposited metal first with water, then with alcohol, and finally with ether. Dry in the usual way and weigh.

After the electrolysis is finished, the solution should always be tested for cadmium. For this purpose, saturate it with hydrogen sulfide. If much cadmium is present, a yellow precipitate is obtained, but if very little, a yellow coloration results. This color, due to the formation of colloidal cadmium sulfide, is so intense that R. Philipp estimates the quantity of cadmium not precipitated by comparing the shade with that produced in a solution containing a known quantity of cadmium and the same amounts of potassium cyanide and caustic potash as in the solution tested.

Remark. If for the electrolysis a current of only 0 5 ampere is used, not all the cadmium will be deposited at the end of 12 hours; if the current is increased at the end to 1 ampere, however, the electrolysis will surely be finished in 6 or 7 hours. To work with the stronger current from the beginning is not to be recommended unless a gauze cathode is used, or one of the electrodes is rotated, for otherwise the metal is deposited in a spongy form and on washing some of it is likely to be lost.

From neutral and weakly acid solutions, cadmium can be deposited electrolytically, but not from strongly acid solutions.

¹ *Ber.*, **12**, 446.

2. Determination as Cadmium Sulfate, CdSO₄

Next to the electrolytic method, the determination of cadmium as sulfate is the best. If the cadmium is combined with a volatile acid, treat the compound in a weighed porcelain crucible with a slight excess of dilute sulfuric acid, evaporate the solution on the water bath as far as possible, and finally remove the excess of sulfuric acid by heating in an air bath (see p. 31). Apply the heat at first slowly, and raise the temperature gradually until finally no more fumes of sulfuric acid are evolved. The outer crucible can even be heated with the full flame of a Teclu burner without running any risk of decomposing the cadmium sulfate; however, it is not necessary to heat it so strongly. As soon as the fumes of sulfuric acid cease to come off, stop heating and weigh the crucible and its contents after cooling in a desiccator. The cadmium sulfate should be pure white and should dissolve in water to form an absolutely clear solution.

If the cadmium has been precipitated from a solution as the sulfide, place the greater part of the precipitate in a large porcelain crucible, cover with a watch glass, and treat with 3 N hydrochloric acid on the water bath. After the precipitate has dissolved and the evolution of hydrogen sulfide has ceased, wash the lower side of the watch glass, place the crucible under the funnel, and dissolve the precipitate which adhered to the filter paper by dropping hot, 3 N hydrochloric acid upon it. Finally wash the filter with hot water and evaporate the solution upon the water bath, continuing as described above.

3. Determination as Cadmium Oxide, CdO

Cadmium carbonate and cadmium nitrate can be changed to the oxide by strong ignition.

To the dilute, boiling cadmium solution add a slight excess of potassium carbonate, and when the precipitate has completely settled after standing for some time on the water bath, filter it off, wash with hot water, and dry. Transfer as much of the dried precipitate as possible to a watch glass and set aside for the time being. Wash the filter with hot 2 N nitric acid to dissolve the precipitate which still adheres to it, and receive the solution in a weighed porcelain crucible. Evaporate to dryness, add the main portion of the precipitate, and heat the crucible at first very gently until the whole mass has become a uniform brown. Now gradually raise the temperature until finally the full heat of the burner is reached. It is important during this operation to take care that the inner flame mantle does not touch the crucible, for

otherwise reducing gases may enter and reduce a part of the oxide to metallic cadmium, which is volatile at this temperature.[1] The cadmium oxide is obtained as a brown powder which is infusible, insoluble in water, but readily soluble in dilute acids.[2]

Remark. It is not advisable to precipitate the cadmium by means of *sodium* carbonate solution, for then it would be difficult to wash the precipitate free from alkali.

4. Determination of Cadmium as Cadmium Pyrophosphate[3]

The cadmium solution used for this method of analysis should not contain ammonium salt other than the reagent and should be faintly acid. If considerable acid is present, neutralize with sodium carbonate solution.

To the cold, faintly acid solution containing not over 0.2 g of cadmium in 100 ml, add a concentrated aqueous solution of $(NH_4)_2HPO_4$ until the weight of added salt is 10–15 times as great as that of the cadmium present. Allow to stand for 12 hours to permit the amorphous precipitate to become crystalline. Filter through a filtering crucible; wash with cold 1 per cent ammonium phosphate solution and finally with 60 per cent alcohol. Heat in an electric oven at 800–900° and weigh as $Cd_2P_2O_7$.

SEPARATION OF THE SULFO BASES FROM THE METALS OF THE SUBSEQUENT GROUPS

Hydrogen sulfide added to a solution which is 0.3 N in acid precipitates only the metals of the "hydrogen sulfide group." It is to be noted that zinc precipitates with this group if the solution is not acid enough, while if the solution is too acid, lead and cadmium are often incompletely precipitated. The following analyses show how the precipitation as sulfide can often be avoided.

EXAMPLE

Analysis of Brass (Alloy of Copper and Zinc Sometimes Containing Small Amounts of Tin, Lead, Iron, and Nickel)

Weigh out 0.4–0.5 g of the alloy into a 200-ml casserole[4] and dissolve in 20 ml of 6 N nitric acid. Cover the casserole with a watch glass to

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[1] If the cadmium carbonate is filtered into a Munroe crucible, and ignited in an electric oven, the transformation takes place readily without danger of any volatilization.

[2] The oxide after ignition is a black, crystalline powder.

[3] Miller and Page, Z. anorg. Chem., 28, 233 (1901).

[4] The borings are often somewhat oily. They should then be washed with ether and dried before weighing.

prevent loss by spattering. After the reaction begins to slacken, heat on the water bath until all the metal is dissolved. Evaporate the solution just to dryness, moisten the residue with a little nitric acid, dissolve in about 50 ml of hot water, and if any metastannic acid settles out on standing filter it off, wash with hot water, dry, and determine the tin according to p. 94. To the cold filtrate add 3 ml of pure, concentrated sulfuric acid, evaporate the solution on the water bath as far as possible, and then heat cautiously over a free flame until dense white fumes of sulfuric acid are evolved. Cool, treat the residue with 50 ml of water and 15 ml of alcohol, stir well, filter, wash, and determine the lead sulfate according to p. 59. Evaporate the filtrate until the alcohol is completely removed, dilute with 100 ml of water, heat the solution to boiling, and conduct hydrogen sulfide into it until it becomes cold. Then filter off the copper sulfide, wash first with hydrogen sulfide water containing, in every 100 ml, 20 ml of 2 N sulfuric acid, and at the end with 5 per cent acetic acid, also saturated with hydrogen sulfide, until the filtrate gives no precipitate on being treated with barium chloride. Heat the filter paper and CuS precipitate in a porcelain crucible until all the paper is consumed and the sulfide oxidized to CuO. Dissolve this in a little 6 N HNO_3, dilute, and electrolyze the resulting solution (p. 69).

Evaporate the filtrate from the copper sulfide to a small volume in order to remove the excess of hydrogen sulfide, oxidize the iron by the addition of bromine water, precipitate by ammonia, and filter. To make sure that the precipitate of ferric hydroxide contains no zinc, redissolve it in a little hydrochloric acid and repeat the precipitation with ammonia. Filter, wash, ignite, and weigh as ferric oxide (cf. p. 152).

Make the combined filtrates from the ferric hydroxide acid with a little sulfuric acid, heat to about 50° C, and determine the zinc as zinc sulfide according to the "salting-out" method described on p. 216. For the determination of nickel, boil the filtrate from the zinc sulfide to expel the hydrogen sulfide and precipitate the nickel as the salt of dimethylglyoxime according to p. 193.

Determination of Copper, Lead, and Zinc in Brass

The best brass alloys contain very little tin, lead, iron, or nickel. In commercial laboratories, often the copper and lead contents are determined electrolytically and the zinc is determined by *difference*, that is, by subtracting the percentages of copper and lead from 100 per cent.

The following method of analysis, however, provides for the determination of copper, lead, tin, iron, and zinc and is capable of giving accurate results.

Weigh 0.9–1.0 g of the alloy into a slender beaker of about 150-ml capacity. Add 12 to 15 ml of 6 N nitric acid, cover the beaker, and heat gently till all the brass is dissolved. If a clear solution is obtained, no tin is present, and the solution after dilution is ready for electrolysis.
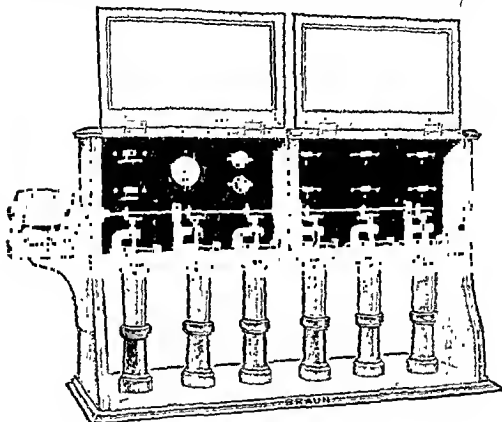
Fig. 24.

If a white precipitate of metastannic acid forms, evaporate the solution just to dryness but do not bake the residue. Add 2 ml of 6 N nitric acid, dilute with 25 ml of water, and boil gently to dissolve the nitrates of copper and zinc. Filter off the metastannic acid, wash it with hot water, ignite in a porcelain crucible, and weigh as SnO_2.

Dilute the clear solution of the nitrates to 100 ml and boil gently for 1 minute to remove any nitrous oxides. Wash down the sides of the beaker and the cover glass, allow to cool a little, and then cautiously add small portions of solid urea until there is no more evolution of gas:

$$2HNO_2 + CO(NH_2)_2 = 3H_2O + CO_2 + N_2$$
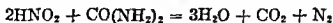
Attach the weighed gauze electrodes to the binding posts of the electrolytic apparatus, put the beaker in place. Make sure that the cathode reaches to the bottom of the beaker and that the anode can rotate freely inside the cathode. Turn on the stirrer and turn the switch with the

rheostat adjusted to give a current of 1.8–2.0 amperes. After the solution has become colorless, continue the electrolysis 10 minutes longer. The electrolysis ought not to require more than 45 minutes at the most.

Wash the electrodes while lowering the beaker and while the current is still flowing. Dip them in alcohol and dry a very short time in the hot closet at 105°. The deposit on the cathode is pure copper, and that on the anode is lead dioxide, PbO_2.

To make sure that all the copper has been deposited, add a slight excess of ammonia to the entire solution. If a blue color is noticeable,[1] make acid with dilute sulfuric acid and electrolyze with clean electrodes until all the copper is removed.

The electrolysis can take place without stirring. In this case use 0.15 ampere of current and electrolyze over night.

Test for Iron and Aluminum

To the electrolyzed solution add a little bromine water, to make sure that any iron is in the ferric condition, and enough ammonia to dissolve the zinc hydroxide precipitate that may form at the neutral point. If any precipitate of ferric or aluminum hydroxide forms, filter it off. To make sure that no zinc hydroxide is in the precipitate, redissolve the precipitate in a little hot 2 N hydrochloric acid, dilute to 50 ml, and precipitate again by adding ammonia. Ignite and weigh the precipitate as Fe_2O_3. If there is any likelihood of aluminum being present, examine the ignited oxides as described on p. 169.

Determination of Zinc

Procedure. To the *cold* acid solution of the zinc salt add ammonium hydroxide until the solution is barely acid to methyl orange. Care is necessary at this point, as zinc ammonium phosphate is soluble both in acids and in ammonia. Sometimes nitrous acid which is present decomposes the indicator and makes it difficult to tell the methyl orange color change. Make sure that the neutralized solution has no appreciable odor of ammonia, after blowing away the fumes. Dilute with water, if necessary, to a volume of 150 ml, and heat on the water bath. To the hot solution add 3 g of $(NH_4)_2HPO_4$ dissolved in a little water. The precipitate that first forms is amorphous and does not settle out, but it soon changes to finely crystalline $ZnNH_4PO_4$ which settles well and leaves a clear supernatant liquid. The transformation takes place more

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[1] A pale blue color may indicate the presence of nickel but usually is caused in brass analysis by a little copper which has escaped deposition

rapidly in proportion to the quantity of ammonium salt present. After the heating has continued for about 15 minutes, remove the dish from the water bath, and when the precipitate has settled for a short time filter off the precipitate into a weighed filtering crucible, wash 6 times with hot 1 per cent ammonium phosphate solution, then twice with cold water, and finally with 50 per cent alcohol. Dry at 100–135° for an hour and weigh as $ZnNH_4PO_4$, which contains 36.64 per cent Zn. The precipitate can be washed and dried with alcohol and ether if desired (cf. p. 83).

The precipitate can also be weighed as the pyrophosphate, $Zn_2P_2O_7$, in which case it is desirable to heat the dried zinc ammonium phosphate very slowly in an electric oven to 900–1000°. If such an oven is not at hand place the filtering crucible in a larger crucible and heat over the gas flame. Gradually raise the temperature until finally the full heat of the Teclu or Méker burner is reached. Heat to constant weight after cooling in a desiccator. Before using the filtering crucible, it must be heated, cooled, and weighed in the same way. $Zn_2P_2O_7$ contains 42.90 per cent Zn.

Test the filtrate from the $ZnNH_4PO_4$ precipitate with ammonia and ammonium sulfide. If a small precipitate of white zinc sulfide is formed, filter it off, using an ashless paper filter, ignite in a porcelain crucible, and weigh as ZnO. No sulfide precipitate will be formed if the above conditions have been followed carefully.

Titrimetric Determination of Lead in Brass

Dissolve 5 g of brass in 50 ml of 6 N HNO_3. (If an appreciable quantity of metastannic acid separates and gives a turbid solution, remove it as directed on p. 74.) To the solution add 15 ml of 18 N H_2SO_4 and evaporate on the hot plate, without boiling, until fumes of H_2SO_4 are evolved. Allow to cool, carefully wash down the sides of the beaker, and again evaporate to fumes Do not cover the beaker tightly during the evaporation because, if water condenses on the bottom of the watch glass and later drops into the hot acid, there will be spattering. After all nitric acid has been expelled by this double evaporation, cool, add 100 ml of water, mix well, add 30 ml of alcohol, and allow to stand at least 1 hour. Filter through a paper filter and wash the precipitate of $PbSO_4$ with 0.7 per cent ammonium sulfate solution or with 1.8 N H_2SO_4.

With the aid of the wash bottle, transfer as much of the precipitate as possible to a 300-ml beaker, replace the funnel, and, with the 300-ml beaker under it, dissolve the $PbSO_4$ on the filter in not more than 25 ml of hot 3 N ammonium acetate solution as follows: Pour about 5 ml of hot acetate solution upon the upper part of the filter and wash with about 10 ml of hot water from the wash bottle. Repeat this treatment three times. Then treat with another portion of ammonium acetate solution and test the filtrate that now runs through the filter with a few drops of K_2CrO_4 solution. If a precipitate forms, save it and continue the treatment with ammonium acetate solution and hot water until a negative test is obtained.

Make the ammonium acetate solution acid with about 2 ml of 6 N acetic acid, heat to boiling, and add 5 ml of 5 per cent $K_2Cr_2O_7$ solution. Boil gently for 5 minutes, filter, and wash 10 times with hot water. The last washings should show no yellow color. Place a clean beaker under the funnel and dissolve the $PbCrO_4$ in 12–15 ml of cold 6 N HCl added in small portions and with intermediate washing with water. The acid must be cold to avoid reducing some of the chromic acid to chromic salt. All yellow color must be removed from the filter, but it does no harm if some white $PbCl_2$ remains. Continue washing until about 100 ml of filtrate has been collected. Add to the solution 2 g of KI, and titrate the liberated iodine with standardized $Na_2S_2O_3$ solution. One milliliter of 0 1 N $Na_2S_2O_3$ = 0 006907 g Pb.

Determination of Copper in Iron and Steel

Dissolve 10 g of sample in 200 ml of 3.6 N sulfuric acid and when the metal is dissolved dilute to at least 500 ml with water. Heat to boiling and saturate with hydrogen sulfide. Filter on paper or paper pulp and wash a few times with a 1 per cent sulfuric acid solution saturated with hydrogen sulfide. Ignite the residue and paper in a porcelain crucible and fuse with 2 to 4 g of alkali pyrosulfate. Dissolve the cooled melt in the crucible in 25 ml of 1.2 N hydrochloric acid and a few milliliters of water, neutralize with 5 per cent sodium hydroxide, and add 0.3 ml in excess. Boil for 3 minutes; digest for 30 minutes, filter and wash with cold 0.2 N NaOH solution. Reserve the filtrate for the determination of molybdenum.

Dissolve the precipitate in 15–25 ml of hot 4 N HNO_3 and wash the filter paper with hot water. Add 5 ml of concentrated sulfuric acid, evaporate to fumes of sulfuric acid, cool, dilute to 40 ml, and add 10 ml of 15 N ammonium hydroxide. This serves to precipitate any iron, chromium, aluminum, etc., and leaves the copper in solution as blue copper-ammonia complex. If there is more than 4 mg of precipitate, dissolve it in 10 to 25 ml of hot 4 N HNO_3 and repeat the treatment with ammonia. Filter and combine the two ammoniacal filtrates. The further treatment depends on whether the copper is to be determined (a) by electrolysis or (b) as oxide.

(a) Transfer the ammoniacal solution to a 150-ml beaker; neutralize with 6 N H_2SO_4 and add 10 ml in excess. Also add 1 g of NH_4NO_3, dilute to 100 ml, and electrolyze with a current of about 0.5 ampere, preferably with stirring. Continue the electrolysis until a few drops of the electrolyte give no darkening with a little H_2S water. Remove and weigh the electrodes as described on p. 69.

(b) Neutralize the ammoniacal filtrates with 6 N H_2SO_4 and add 5 ml in excess. Heat to boiling, and saturate with H_2S as the solution cools. Digest for about 15 minutes, filter, wash, ignite, and weigh as CuO as described on p. 66.

Remark. If the steel contains tungsten, tungstic acid will separate out from the original solution and will carry some copper down with it. With tungsten steels the following procedure should be used.

Dissolve 10 g of steel in 100 ml of 6 N HCl. To the solution add 25 ml of 6 N HNO$_3$ and boil until the separated tungstic acid, H$_2$WO$_3$, is yellow. Dilute to 150 ml with boiling water. After a few minutes filter and wash the residue with 1.2 N HCl. Examine both filtrate and precipitate for copper.

Dissolve the precipitate in hot N NaOH solution. To the solution add 5 g of tartaric acid and sufficient 6 N H$_2$SO$_4$ to make the solution about 0.3 N in free H$_2$SO$_4$. Heat the solution and precipitate with H$_2$S as described above.

To the filtrate from the first filtration, add 10 ml of concentrated H$_2$SO$_4$ and evaporate until fumes of SO$_3$ are evolved. Cool, heat to boiling, and filter if necessary, finally washing with 2 N H$_2$SO$_4$. To the solution add tartaric and sulfuric acids as above and precipitate the copper with H$_2$S.

Analyze the combined CuS precipitates as described for steels containing no tungsten.

SEPARATION OF THE SULFO BASES FROM ONE ANOTHER

1. Separation of Mercury from Lead, Bismuth, Copper, and Cadmium

Method of Gerhard v. Rath

Principle. This separation is based upon the insolubility of mercuric sulfide in boiling 6 N nitric acid and the solubility of the remaining sulfides in this acid.

Procedure. The solution must contain the mercury entirely in the mercuric form and should be 0.3 N in hydrochloric or sulfuric acid. Into the hot, fairly dilute solution introduce hydrogen sulfide in excess. Filter off the precipitate, wash it with hydrogen sulfide water, transfer to a porcelain dish, and boil for a considerable length of time with 6 N nitric acid. Then dilute with a little water and wash with water containing nitric acid. The residue of mercuric sulfide thus obtained always contains sulfur, and if considerable lead was present it may also contain lead sulfate. Dissolve it, therefore, in a little aqua regia, dilute with water, filter from the separated sulfur and lead sulfate, and precipitate the mercury with ammonium sulfide (cf. p. 54) according to the method of Volhard. If some of the lead sulfate should go into solution with the mercury on treating with aqua regia, it will be converted by the ammonium sulfide and potassium hydroxide into insoluble lead sulfide, while the mercury will be in the form of its soluble sulfo salt. In this event filter off the lead sulfide, wash with dilute potassium hydroxide solution, and precipitate the mercury as sulfide, as described on p. 54.

2. Separation of Bismuth from Lead

(a) Method of Löwe[1]

Principle. Bismuth nitrate is changed by the action of water into an insoluble basic salt, but lead nitrate undergoes no such transformation.

Procedure. Evaporate the nitric acid solution of these two metals on the water bath until it reaches a sirupy consistency. Add water, and after thorough stirring with a glass rod repeat the evaporation and continue this treatment until the addition of the water fails to produce any further turbidity, a sign that the bismuth has been completely converted into the basic salt $Bi_2O_2NO_3OH$. Add 100 ml of a cold 2 per cent ammonium nitrate solution, and after standing some time, with frequent stirring to make sure that the lead nitrate is completely dissolved, filter the solution. Wash the precipitate with the dilute ammonium nitrate solution and dry. Transfer as much of it as possible to a weighed porcelain crucible, burn the filter and add the ash to the crucible, and ignite to a constant weight of Bi_2O_3.

From the filtrate precipitate the lead as sulfate, according to p. 58, and weigh as such.

(b) Method of Ledoux[2]

To 100 ml of the dilute nitric acid solution, add 6 N NH$_4$OH dropvise from a buret until a faint opalescence appears. Then add 1 cc of 3 N HCl, dilute to 300 ml, and heat just to boiling. Allow to stand on the steam bath for 2 hours or in a warm place over night. Filter off the precipitate of BiOCl and possibly SbOCl and a little PhCl$_2$, and wash the precipitate twice with boiling water. Dissolve it in a little 3 N HCl, and to the solution add an amount of water about 30 times as large as the amount of the acid used. If a precipitate appears on dilution, pay no attention to it. Saturate with hydrogen sulfide and filter off the Bi$_2$S$_3$ precipitate, which may contain Sb$_2$S$_3$ and a little PhS. Wash this precipitate once with water, twice with hot, diluted ammonium sulfide reagent to remove antimony, and then with more water. Dissolve the precipitate in a little hot 3 N HNO$_3$, washing the filter paper with this acid and finally with hot water. Dilute and reprecipitate

[1] *J prakt. Chem.*, 74, 345 (1858). Cf. Little and Cahen, *Analyst*, 35, 301.

[2] A H. Low, *Technical Methods of Ore Analysis*, Hillebrand-Lundell, *Applied Inorganic Analysis*

the BiOCl exactly as described above. Dry at 100°, and weigh as BiOCl.

3. Separation of Bismuth from Copper

To the dilute solution add an excess of ammonium carbonate solution, heat gently, and filter. The precipitate of basic bismuth carbonate almost always contains small quantities of copper; redissolve it in nitric acid and repeat the separation by means of ammonium carbonate. Fuse the basic bismuth salt with potassium cyanide, leach with hot water and treat the residual bismuth according to p. 63.

For the copper determination, combine the two filtrates, evaporate to remove the excess of ammonium carbonate, make acid with sulfuric acid, and precipitate the copper by means of hydrogen sulfide. Weigh the copper as cuprous sulfide according to p. 67, or electrolyze the sulfuric acid solution as described on p. 69.

According to Fresenius and Haidlin, bismuth can be separated from copper very satisfactorily by means of potassium cyanide. For this purpose, treat the acid solution with a slight excess of sodium carbonate, add potassium cyanide, heat the solution, and filter. All the copper is found in the filtrate, while the precipitate contains bismuth oxide contaminated with alkali. Dissolve the residue, therefore, in nitric acid, precipitate the bismuth by means of ammonium phosphate, and determine as phosphate according to p. 63. Evaporate the filtrate containing the copper with nitric acid, to destroy the cyanide, and determine copper electrolytically according to p. 69.

Another method of carrying out the separation of bismuth from copper by means of KCN is to heat a mixture of the freshly precipitated sulfides with a solution of 3 to 4 g of KCN in a little water. Bi_2S_3 remains undissolved.[1]

4. Separation of Lead from Copper by Means of Electrolysis

This separation depends upon the fact that the electric current deposits lead quantitatively as PhO_2 upon the anode from solutions containing considerable nitric acid, while the copper is either not deposited at all under these conditions or is found upon the cathode to some extent. After the lead is completely deposited, the copper solution is poured into a second weighed platinum dish, the excess of the acid is neutralized with ammonia, and the solution is again electrolyzed. The copper will now deposit quantitatively upon the cathode. The procedure has already been described (cf. pp. 62 and 69).

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[1] A. H. Low, *Technical Methods of Ore Analysis*.

5. Separation of Lead from Copper and Cadmium

(From Bismuth Less Satisfactorily)

To the solution of the nitrates or chlorides add an excess of sulfuric acid, evaporate to remove the nitric or hydrochloric acid, and determine the lead as sulfate as described on p. 58.

6. Separation of Copper from Cadmium

(a) By Electrolysis

The solution should contain not more than 0.2 g of cadmium. To the neutral solution add 10 ml of 6 N nitric acid, dilute to 150 ml in a platinum dish, and electrolyze with the dish as cathode. Adjust the anode, a disk electrode, so that it dips into the liquid only a short way. Under these conditions, 0.2 g of copper is deposited, perfectly free from cadmium, within 12–14 hours by a current of 0.2–0.3 ampere at a voltage of 1.9–2.3 volts. With a current of 1–1.5 amperes and 2.5–2.6 volts electrode potential, the copper is deposited in about 5 hours. When the deposition is complete, siphon off the solution while pouring pure water into the dish without breaking the current. Finally rinse the dish with alcohol, dry, and weigh with the deposited copper. Add a little sulfuric acid to the solution, evaporate to expel the nitric acid, cool, dilute, and electrolyze the cadmium from cyanide solution as described on p. 70.

Remark. If considerably more than 0.2 g Cd is present in 150 ml of the solution, there is danger of small amounts of cadmium separating out upon the copper during the washing of the deposit, especially if the anode extends well into the solution. This is because the concentration of the acid becomes less during the washing. In analyzing a solution containing a large amount of cadmium and small amount of copper, therefore, it is best to wash at first with 2 per cent nitric acid rather than with distilled water.

The separation requires but a few minutes with a rotating anode or cathode, and a stronger current.

F. Foerster recommends the following conditions for an electrolytic separation of copper and cadmium: Electrolyte: 100 ml of 2 N sulfuric acid. Electrodes: a large platinum gauze electrode as cathode and a smaller one as anode. Connect the electrodes directly with the terminals of a single storage cell so that the voltage is kept constant throughout the electrolysis. After 60–90 minutes 0.2 g of copper will be deposited completely. Remove the cathode in the usual way (p. 69), neutralize the solution with potassium hydroxide solution, add potassium cyanide, and electrolyze for cadmium according to directions on p 70.

(b) Method of Rivot-Rose

Precipitate the copper as thiocyanate according to p. 68, and in the filtrate precipitate cadmium as sulfide and determine as sulfate according to p. 71. The results are good.

(b) ELEMENTS THAT FORM SULFIDES INSOLUBLE IN DILUTE MINERAL ACIDS BUT SOLUBLE IN SOLUTIONS OF ALKALI SULFIDE (THE SULFO ACIDS)

ARSENIC, ANTIMONY, TIN, GERMANIUM, MOLYBDENUM, SELENIUM, TELLURIUM

ARSENIC, As.   At. Wt. 74.91

Forms: As_2S_3, As_2S_5, $Mg_2As_2O_7$

The three best ways of determining arsenic are (1) the gravimetric determination as As_2S_3 (see below); (2) the volumetric determination of the silver in a precipitate of Ag_3AsO_4 (see Chapter XVII, Procedure 21); and (3) the iodimetric titration of trivalent arsenic in a buffered solution (see Chapter XV).

1. Determination as Arsenic Trisulfide, As_2S_3

For the determination of arsenic in this form, it must be present in its trivalent state, i.e., as arsenious acid or as arsenite.

Make the solution strongly acid with hydrochloric acid and precipitate the arsenic in the cold with hydrogen sulfide. Remove the excess of hydrogen sulfide by a stream of carbon dioxide, and filter through a Gooch crucible that has been previously dried at 105°. Wash the precipitate with hot water, dry at 105° to constant weight, and weigh as As_2S_3.

2. Determination as Arsenic Pentasulfide, As_2S_5, according to Bunsen[1]

Modified by Fr. Neher[2]

To the solution, which must contain all the arsenic as arsenic acid, add 12 N hydrochloric acid little by little (it is best to keep the solution cooled by surrounding the flask with ice) until the solution is at least 4 N in hydrochloric acid. Conduct a very rapid stream of hydrogen sulfide into this solution (contained in a large Erlenmeyer flask) until it is saturated with the gas. Then stopper the flask and allow to stand 2 hours. Filter off the arsenic pentasulfide through a Gooch crucible which has been dried at 105°, and wash the precipitate thoroughly with water, then with hot alcohol (to hasten the subsequent drying). After drying at 105° weigh the precipitate as As_2S_5. It is not necessary to wash it with carbon bisulfide.

[1] Ann. Chem. Pharm., 192, 305.
[2] Z. anal. Chem., 32, 45; see also Brunner and Tomicek, Monatsh., 8, 607; McCay, Z. anal. Chem., 27, 682, and J. Thiele, Ann. Chem. Pharm., 265, 65.

Remark. If the above directions are followed exactly, this method gives faultless results. If, on the other hand, the directions are deviated from in the slightest respect, the precipitate is likely to contain some arsenic trisulfide, whereby low results will be obtained. If the solution is not kept cool and the hydrochloric acid is added too rapidly, the heat of the reaction suffices to change a part of the arsenic pentachloride (this compound probably exists in solution) to arsenious chloride and chlorine, so that on passing hydrogen sulfide into the solution a mixture of arsenic trisulfide and arsenic pentasulfide will be obtained.

3. Determination of Arsenic as Magnesium Pyroarsenate, according to Levol

The solution must contain all the arsenic as arsenate, and have a volume of not more than 100 ml per 0.1 g arsenic. Add 5 ml of 12 N hydrochloric acid drop by drop, with constant stirring, and then, for each 0.1 g of arsenic, add 7-10 ml of magnesia mixture[1] and a drop of phenolphthalein indicator solution. Now, with constant stirring, add 6 N ammonia from a buret until the phenolphthalein imparts a permanent red color to the solution, and then add enough more ammonia to make one-third the volume of the neutralized solution. After the liquid has stood for 12 hours filter it through a Gooch or Munroe crucible. Transfer the precipitate in the beaker to the crucible by some of the original solution blown from a small wash bottle. Wash the precipitate with 1.5 N ammonia solution containing 2-3 per cent of ammonium nitrate until free from chloride. Drain the crucible as completely as possible by suction, dry at 100°, and heat in an electric oven quite gradually to a temperature of 400° to 500°, until no more ammonia is evolved. Then raise the temperature to 800-900° and keep there for about 10 minutes. Cool the crucible in a desiccator and weigh as $Mg_2As_2O_7$.

If an electric oven is not available, place the crucible with the precipitate in an air bath (cf. p. 31). Sprinkle a thin layer of powdered ammonium nitrate[2] upon the precipitate, and heat, gently at first, gradually increasing the temperature until the outer crucible is light red. Cool in a desiccator and weigh as $Mg_2As_2O_7$. The results obtained are excellent.

Remarks. The precipitate produced by the magnesia mixture has the formula $MgNH_4AsO_4 \cdot 6H_2O$ and loses $5\frac{1}{2}$ molecules of water at 102°; it has, therefore, been proposed to weigh the precipitate after drying at this temperature. Better results are obtained by washing the precipitate with 1.5 N NH_4OH until free from chloride then with four 5-ml portions of alcohol followed by four 5-ml portions of ether and

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[1] Dissolve 55 g crystallized magnesium chloride and 70 g ammonium chloride in 650 ml water and dilute to a volume of 1 l with 6 N NH_4OH.

[2] Instead of using ammonium nitrate, the crucible may be provided with a perforated cover and heated in a current of oxygen.

weighing as $MgNH_4AsO_4 \cdot 6H_2O$ (cf. Chapter V, "Magnesium"). According to J. F. Virgili[1] it requires 25 l of 1 5 N ammonia to dissolve 1 g of the precipitate. A precipitate of As_2S_3 or of As_2S_5 can be analyzed by the above method after treating the precipitate with HCl and $KClO_3$ as in qualitative analysis.

4. Colorimetric Determination of Arsenic

Fig. 25:

Small quantities of arsenic can be estimated very accurately by means of the Marsh apparatus, comparing the mirror with a series of standards formed with known quantities of arsenic.[2] It is nearly as accurate, however, to use the much simpler apparatus recommended for the Gutzeit test. Treadwell and Comment[3] allowed the arsine to react with disks containing silver nitrate and compared the resulting color with standards which, unfortunately, must be produced freshly with each analysis, as they do not keep very well. Almost equally accurate and much more convenient are the methods of F. Hefti[4] and of C. R. Sanger and O. F. Black[5] in which the arsine is made to react with mercuric chloride paper.

Oxidizing agents and compounds that yield H_2S, SO_2, or H_3P should be absent. The last three, as well as organic matter, can be removed by heating with concentrated HNO_3 and fuming with H_2SO_4 (cf. p. 167). The presence of Fe^{++} and $SnCl_2$ is advantageous; less than 0.1 g Sb does not interfere.

The formation of AsH_3 takes place in a wide-mouth bottle of about 60-ml capacity (Fig. 25) which is fitted with a one-hole rubber stopper carrying the tubes A, B, and C. The tube A contains dry strips of lead acetate paper which serve to remove H_2S formed from a little sulfur in the zinc used. The tube B is packed loosely with glass wool that has been moistened with lead acetate solution. The tube C contains a piece of filter paper impregnated with mercuric chloride. The test papers and reagents are prepared as follows:

Ferric Alum Solution. Dissolve 8.4 g of ferric ammonium alum in water containing 1 g NaCl and 2 ml of concentrated H_2SO_4 and dilute to 100 ml

Lead Acetate Solution. Dissolve 1 g of $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ in water, add sufficient acetic acid to clear the solution, and dilute to 100 ml.
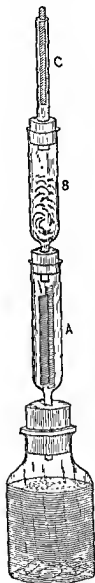
[1] Z. anal. Chem., 44, 504 (1905).

[2] C. R. Sanger, Am. Chem. J., 13, 431 (1891); Z. anal. Chem., 38, 137 and 377; G. Lockemann, Z. angew. Chem., 1905, 429 and 491.

[3] This method was given in the early editions of this book.

[4] Inaug. Dissert. Zurich, 1907.

[5] Proc. Am. Acad. Arts and Sci., No. 8, 1907; J. Soc. Chem. Ind., 26, 1115 (1907).

Cf. Allen and Palmer, 8th Int. Congr. Appl. Chem., 1–2 [I–II], 9 (1912).

Zinc. Treat zinc, free from arsenic and preferably of $\frac{1}{8}$- to $\frac{1}{3}$-inch mesh, with hydrochloric acid until the surface is clean, wash with water, and keep under water.

Stannous Chloride. Dissolve 8 g of $SnCl_2 \cdot 2H_2O$ in 9 5 ml of water and 0.5 ml of concentrated HCl.

Lead Acetate Paper. ·Soak qualitative filter paper in the lead acetate solution, dry, and cut into strips about 7 cm by 5 cm.

Sensitized Test Papers. Prepare strips of uniform 4-mm width from clean, cold-pressed drawing paper which weighs about 160 g per square meter. Such strips can be purchased. Thoroughly soak by drawing the strips through a saturated mercuric chloride solution (about 5 g $HgCl_2$ per 100 ml), dry on a rack of glass rods, and cut into 7-cm lengths; discard the ends by which the strips were held during the immersion in $HgCl_2$ solution.

Standard Stains. Prepare a set of standard test papers by volatilizing known quantities of arsenic as AsH_3 by the same method as that followed in the analysis. The standards can range from 0.001 mg (or 1γ) to 0 050 mg of As. The stains fade when exposed to moist air but when coated with paraffin can be kept for some days in a desiccator in the dark. For preparing the standards, dissolve 20 mg of As_2O_3 in 10 ml of N NaOH by heating. Dilute to exactly 1 l and mix. For less than 0.02 mg of As_2O_3 (1 ml of the standard solution) dilute the solution tenfold.

Procedure. Place 50 ml of the solution to be tested (which can be an aliquot part of the main solution) in the 60-ml decomposition flask and add 2.5 ml of concentrated sulfuric acid, 2 ml of the ferric alum solution, and 0.5 ml of the stannous chloride solution. Heat, if necessary, to about 25°, add 35 g of the arsenic-free zinc, insert the stopper carrying the three tubes properly filled, shake gently, and allow the apparatus to stand for an hour with the solution kept in a bath at 25°. Then remove the test paper and compare the stain with the standards. If the standards have been covered with paraffin, cover the test with paraffin in the same way.

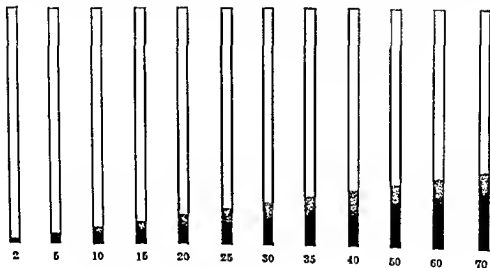Figure 26 shows how the yellowish brown stained test strips should look.

FIG. 26.

ioto the glass tubing of H, thus preventing loss of arsine through this tubing. Outside of this cathode compartment place an ordinary platinum gauze electrode to serve as anode. The absorption flask J should contain 25 ml of 0.1 N iodine solution, and it should be connected with a similar absorption flask cootaioing 25 ml of 0.1 N thiosulfate. Both solutions must be measured carefully from a pipet or buret.

Procedure. The arsenic solution to he tested must contain all the arsenic in the trivalent condition. Pour 4 N sulfuric acid into the heaker and cover the anode with this electrolyte. Pour the solution to be tested for arsenic into the cathode compartment and have the level of the sulfuric acid in the heaker about 2 cm higher than that of the solution around the catbodc. After this dilution, the solution should not contain more than 0.08 g As_2O_3 in 50 ml. Close the cathode compartment with a stopper carrying the cathode and the gas delivery tubing. Place the heaker in ice water to keep the temperature below 10°, and electrolyze as described below. Apply gentle suction at tbe end of the absorption, close the electric circuit, and use 2–3 amperes of current. Regulate the suction so that hubble after hubble of air slowly streams tbrough tbe pressure regulator and into the cathode compartment throughout the duration of the electrolysis. Moreover, take care that sufficient ice remains in the cooling bath. When all the conditions are maintained satisfactorily, the liquid in the cell should remain perfectly clear, or at the worst be colored only by a slight brownish turbidity which eventually disappears. If a black turhidity is formed that scttles to the bottom of the U-tube, something has gone wrong and it is useless to continue the experiment. In a normal experiment, the evolution of the arsine is finished in an hour, if not more than 50 mg of As_2O_3 is present. Then turn off the current and pour the contents of the two absorption tubes (first the iodine and then the thiosulfate solution) into a heaker containing 5 ml of a saturated solution of pure $NaHCO_3$. Titrate tbe excess iodine with 0.1 N sodium thiosulfate solution in the presence of starch solution as indicator. If on mixing the contents of the two absorption hulbs the solution is decolorized, finish the titration with 0.1 N iodine (cf. " Iodimetry ").

This method ean he carried out very easily aod gives accurate results in the presence of iroo, so that it is suitable for a rapid determination of the arsenic present in iron minerals.

Fuse 1 g of powdered mineral m a nickel crucible with 6 g Na_2CO_3 and 1 g of KNO_3. Digest the melt with dilute sulfuric acid, filter, and to the filtrate add 200 ml of saturated SO_2 solution; boil to expel excess SO_2, dilute to make about 2 N io H_2SO_4, and use a suitable aliquot for the electrolysis.

ANTIMONY, Sb. At. Wt. 121.76

Forms: Sb_2S_3, Sb_2O_4, and Sb

1. Determination as Trisulfide, Sb_2S_3

(a) Method of F. Henz[1]

Conduct hydrogen sulfide for 20 minutes into the cold solution, which should be about N in HCl, then, without stopping the current of hydrogen sulfide, slowly heat the solution to boiling and continue the stream of hydrogen sulfide for 15 minutes more. Remove the flame, allow the precipitate to settle, and decant through a Gooch crucible which has been heated at 280–300° and weighed. Wash the precipitate four or five times by decantation with 50–75 ml of hot, very dilute acetic acid into which hydrogen sulfide has been passed. Wash on the filter with the same liquid until all chloride is removed. At first the filtrate runs through perfectly clear, but after all the mineral acid has been removed, the filtrate shows a slightly orange tint, owing to an unweighable amount of the antimony sulfide passing through in colloidal solution. As soon as this point is reached, stop the washing.[2]

Place the crucible, after the precipitate has been dried as much as possible by suction, in the tube R, Fig. 29, which is fitted to a drying oven (about 18 cm long and 10 cm high and covered with asbestos paper). Close the tube R with

FIG. 29.

a rubber stopper that holds a glass delivery tube, and push R into the drying closet until the end of the stopper is reached. To protect the

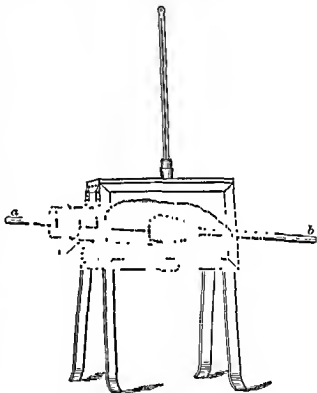[1] F. Henz, Z anorg Chem , 37, 18 (1903).

[2] This precipitate can be used advantageously for the volumetric determination of antimony (see Analysis of Stibnite)

rubber stopper during the subsequent heating, fit a Rose crucible cover against it, holding it in place by wrapping the tube a with a strip of asbestos paper.

Expel all air from the tube by a stream of dry, air-free carbon dioxide and heat for 2 hours at 100° to 130°. Inasmuch as the tube R extends so far into the drying oven, there is no danger of water condensing in the tube; it is all expelled as vapor at b. The precipitate is now dry and the air completely expelled from the heating tube.

Now withdraw the tube R a little way out of the oven, about 5 cm, as shown in the drawing, raise the temperature to 280–300°, and keep it there for 2 hours.

Hereby some sulfur is volatilized and collects in the tube R outside the oven. The orange pentasulfide is also completely changed into the black antimony trisulfide by this heating.[1] Allow the crucible to cool in the stream of carbon dioxide, transfer to the balance case,[2] let stand half an hour, and weigh. The black antimony trisulfide is not at all hygroscopic. A further heating in the current of carbon dioxide will rarely show any change in weight.

(b) Method of Vortmann and Metzl[3]

When antimony is precipitated by hydrogen sulfide from a hot solution which is strongly acid with hydrochloric acid, the sulfide eventually becomes grayish black in color, is crystalline, and can be filtered easily and washed with water without the slightest tendency to pass into the hydrosol condition.

To each 100 ml of neutral solution in an Erlenmeyer flask, add 24 ml of 12 N hydrochloric acid. Heat to boiling, and subject the hot solution to the action of hydrogen sulfide gas. Place the Erlenmeyer flask containing the solution in a dish of boiling water and keep the water boiling during the precipitation. It is advisable to introduce the hydrogen sulfide gas quite rapidly at first, but towards the end a slow stream is sufficient. The antimony sulfide as it comes down is yellow at first, but as the precipitation proceeds, it becomes redder; gradually it becomes heavier and denser, assumes a crystalline form and becomes

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[1] According to Paul (Z. anal. Chem., **31**, 540 (1892)), the transformation of antimony pentasulfide can be accomplished at 230° but it is much more rapid at 280–300°. It is more difficult to replace the air completely with carbon dioxide in Paul's drying oven.

[2] Roll up a piece of writing paper and place it in the tube R, so that the crucible does not come in contact with any of the sulfur sublimate, on withdrawing it. Remove the crucible with the paper.

[3] Z. anal. Chem., **44**, 526 (1905)

darker and finally black in color. The transformation into the crystalline form is hastened by shaking the flask. At first, while the precipitate is of a yellowish color, there is no need for shaking the flask, but later on it is very desirable to do so. The shaking, however, should not be too violent, as otherwise some of the precipitate is likely to adhere to the upper portions of the flask and escape the transformation. The reaction requires 30–35 minutes. Finally a heavy, dense, crystalline precipitate of antimony trisulfide is obtained which settles well and permits of a rapid filtration. Dilute the solution with an equal volume of water, allowing it to flow around the walls of the flask in order to wash down any adhering sulfide. The dilution almost always causes the formation of a slight yellow turbidity. The reason for this is that a little of the antimony is held in solution by the strong acid and as the solution is diluted this is caused to precipitate by the dissolved hydrogen sulfide. Once more shake the flask, replace it in the vessel of boiling water, and introduce more hydrogen sulfide. In 2 or 3 minutes the solution above the precipitate will become clear. Filter through a Gooch crucible, wash with water to remove the acid, then with alcohol, place in the drying oven, and heat as described under (a).

2. Determination as Tetroxide, Sb_2O_4 (Bunsen)

This method is based upon the fact that antimony pentoxide, when ignited at a definite temperature, changes into Sb_2O_4. Bunsen,[1] who first proposed the method, later abandoned it because his assistant succeeded in volatilizing more than 0.1 g of the precipitate by heating it over the blast lamp.[2] Brunck,[3] Rössing,[4] and Henz[5] have shown, however, that accurate results can be obtained. In 1897, Baubigny[6] discovered that antimony pentoxide is converted quantitatively into the tetroxide at a temperature of 750–800°. The literature is conflicting with regard to the volatility of Sb_2O_4. This oxide can be regarded as antimonous antimonate with one atom of antimony in the trivalent condition and the other atom in the quinquevalent state. The oxide Sb_2O_4 is very easily reduced and Sb_2O_3 volatilizes quite rapidly at 1000° (0.35 g in 30 minutes).

Procedure. Ordinarily it is desired to determine the amount of antimony present in a mixture of its tri- and pentasulfides, or in a mixture of one or the other of the two compounds with sulfur. It is best to proceed as follows: Precipitate the sulfide of antimony from a hot solution, wash the precipitate first with hot water, then with alcohol,

[1] *Ann. Chem. u Pharm*, 106, 3 (1858).

[2] *Ibid*, 192, 316 (1878).

[3] *Z anal Chem.*, 34, 171 (1895).

[4] *Ibid.*, 41, 9 (1902).

[5] *Loc. cit.*

[6] *Compt. rend.*, 124, 499 (1897).

afterwards with a mixture of alcohol and carbon disulfide (in order to remove the sulfur),[1] again with alcohol, and finally with ether. Then dry the precipitate, separate the bulk of the precipitate from the filter, and place it upon a watch glass. Put the filter in a small porcelain dish and boil it with a little freshly prepared ammonium sulfide solution, stirring constantly with a glass rod. Pour the resulting solution through a small filter into a 30-ml porcelain crucible, and treat the filter repeatedly with ammonium sulfide solution until it is no longer brownish red at the edge of the paper, where it begins to dry; the extraction of the antimony sulfide is then complete. Evaporate the solution in the crucible to dryness and add the main part of the precipitate. To oxidize the antimony sulfide, Beckett places the crucible, with a dish of fuming nitric acid beside it, under a bell jar and allows it to stand over night. The vapors of fuming acid slowly oxidize the precipitate in the crucible, and the next morning it is possible to complete the oxidation by means of nitric acid (d 1.4) without the reaction being too violent. Heat the crucible on the water bath until the precipitate becomes white and the greater part of the acid is expelled. Add a little water and, with stirring, enough concentrated ammonia to give an alkaline reaction. Evaporate the contents of the crucible to dryness on the water bath, carefully heat in an air bath (p. 31) until no more fumes of sulfuric acid are evolved, and then for half an hour at 800° in an electric oven. Cool in a desiccator, transfer the crucible quickly to a glass-stoppered weighing beaker, allow to stand 20 minutes in the balance case, and then weigh. Repeat the ignition and weighing until a constant weight is obtained.

3. Determination of Antimony as Metal

The decomposition potential of trivalent antimony cations is below that of hydrogen ions so that it is possible to deposit antimony from acid solutions. By regulating the cathode potential, Sand[2] succeeded in depositing 0.3 g Sb in the presence of considerable H_2SO_4; in the presence of a suitable depolarizer such as $NH_2OH·HCl$ it is possible to deposit antimony from HCl solutions.[3] In general, however, it is preferable to deposit the metal from an alkali sulfide solution.[4]

If a solution of sodium or ammonium thioantimonite, or thioantimonate, containing not more than 0.2 g Sb in a volume of about 140 ml is subjected to electrolysis with

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[1] Thiele, *Ann. Chem. und Pharm.*, **253**, 372.

[2] *Trans. Chem. Soc.*, **93**, 1572 (1908).

[3] Wölbling, *Chem. Analyse*, 17/18, *Chem.*
Soc., **38**, 1660 (1916); Engelenburg, *adwell,*
Elektroanalyt. Methoden.

[4] Parrodi and Mascazzini, *Z. anal. Chem.*, **18**, 587 (1879); (1880); Classen and Reis, *Ber.*, **14**, 1629 (1821), 17, 2467 (27, 2060 (1894).

a current of 1–1.5 amperes at 65° for 90 minutes, the antimony will be deposited upon a platinum dish, which has been etched by treatment with dilute aqua regia, as steel-gray, metallic antimony, and the deposit adheres so firmly that it can be dried and weighed without loss. The chief condition for the success of this operation is the absence of polysulfides. If these substances are present the antimony is incompletely deposited and sometimes not at all, or the deposited antimony may pass into solution, on account of being oxidized to sodium thioantimonite by means of the sodium polysulfide which is formed at the anode during the electrolysis: $2Sb + 3Na_2S_2 = 2Na_3SbS_3$.

It is necessary, therefore, to prevent the formation of polysulfides during the electrolysis. For this reason Lecrenier[1] added sodium sulfite to the bath, whereby the polysulfide is transformed into thiosulfate: $Na_2S_2 + Na_2SO_3 = Na_2S_2O_3 + Na_2S$

Ost and Klapproth[2] carry out the electrolysis with the aid of a diaphragm to keep the polysulfide away from the cathode.

It is better, however, to make use of potassium cyanide for this purpose.[3] $Na_2S_2 + KCN = Na_2S + KCNS$.

Procedure. Usually the antimony is first isolated as the sulfide, which is either precipitated by hydrogen sulfide from acid solution or obtained by acidifying an alkaline solution of the thio salt. Dissolve the filtered and washed precipitate, corresponding to not over 0.2 g Sb, in about 80 ml of a 12 per cent sodium sulfide solution (d 1.14). Transfer the solution to a weighed platinum dish with sand-blasted inner surface. Dilute the solution with 30 ml of 30 per cent freshly prepared pure potassium cyanide solution, and dilute to 125 ml. Heat to 65° (not over 70°) and electrolyze with a current of 1.2–1.3 amperes at an electrode potential of 1.1 to 1.4 volts. After 1.5–2 hours all the antimony will be upon the cathode in the form of a firmly adhering, light gray deposit.[4] Now, without breaking the circuit, siphon off the electrolyte, while adding water until the current ceases to pass through the liquid (the voltmeter connected as ammeter points to the zero reading). Remove the cathode, wash thoroughly with water, then with 95 per cent alcohol, dry at about 80°, cool in a desiccator, and weigh. The results by this method are usually a little high.

Cleaning the Electrodes. Ost[5] recommends heating with a mixture of equal parts concentrated nitric acid and a saturated solution of tartaric acid. The antimony will also dissolve readily by heating with a solution of alkali polysulfide.

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[1] A. Lecrenier, *Chem. Ztg.*, 13, 1219 (1889).

[2] *Z. angew. Chem.*, 1900, 828

[3] Cf. A. Fischer, *Ber.*, 36, 2048 (1903); *Z. anorg. Chem.*, 42, 363 (1904); Hollard, *Bull. soc. chem.*, 23 [3] 292 (1900); F. Henz, *Z. anorg. Chem.*, 37, 31 (1903).

[4] To make sure that the deposition is complete, the liquid may be transferred quickly to a second dish and electrolyzed for half an hour longer. It is seldom that any gain in weight will be shown by this dish.

[5] *Z. angew. Chem.*, 1901, 827.

Tin, Sn.   At. Wt. 118.7

Forms: SnO₂, Sn

1. Determination as Tin Dioxide, SnO₂

Two cases are to be distinguished:

    (a) *The Tin Is Present as Metal (in an Alloy)*.

    (b) *The Tin Is Present in Solution*.

(a) Tin in Brass or Bronze[1]

Procedure. Digest 1.0 g of borings in a small beaker with 25 ml of 6 N nitric acid. Evaporate the solution slowly to about 5 ml but not to dryness. Dilute with water to about 50 ml; heat nearly to boiling and keep at about 90° for at least 20 minutes. Add ashless filter paper pulp (p. 151) and filter while hot. If the filtrate is turbid, refilter and add more filter paper pulp if necessary. Usually only the first 10-15 ml of filtrate will require refiltering. Wash the precipitate at least 10 times with hot 1 per cent ammonium nitrate solution. Place the filter and its contents in a weighed porcelain crucible; heat carefully at first and finally over a Méker burner, over a blast lamp, or in a muffle furnace at 1100°. Weigh as SnO₂.

The tin precipitate invariably contains small quantities of other oxides, and, if there is much precipitate, purification by one of the two following methods is advisable.

(α) After weighing, add to the precipitate six times as much of a mixture consisting of equal parts sodium carbonate and pure sulfur. Heat in a covered porcelain crucible over a small flame until the excess of sulfur is almost entirely removed. This point is easily recognized by there being no longer any odor of SO₂ and no blue flame of burning sulfur evident between the cover and the crucible. Cool and dissolve the melt in a little hot water; the tin goes into solution[2] as sodium thiostannate (cf. Vol. I), together with some copper and iron. Treat the deep brown liquid, therefore, with sodium sulfite[3] solution until it becomes only

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[1] The method is applicable only for alloys which are completely oxidized or dissolved by HNO₃ and which contain no antimony. It is not applicable to Babbitt metal. Antimony behaves like tin in this procedure.

[2] Frequently a single fusion with sodium carbonate and sulfur is insufficient; this is recognized by obtaining a sandy residue insoluble in water. If such a residue appears, filter it off, wash, dry, and repeat the fusion.

[3] The sodium sulfite changes the sodium polysulfide to monosulfide, in which copper and iron sulfides are insoluble.

slightly yellow in color; any iron or copper, etc., will now be precipitated quantitatively as sulfides. Filter off the latter and wash first with water to which a little sodium sulfide has been added and finally with hydrogen sulfide water. As a rule the amount of insoluble sulfide formed by this treatment is so small that after drying it can be ignited in an open porcelain crucible and changed to oxide without introducing any appreciable error. If this weight is subtracted from the original amount of impure stannic oxide, the weight of pure stannic oxide will be obtained. If, however, the amount of impurity present with the residue of metastannic acid is large, the different metals must be separated according to one of the methods for the separation of the sulfo bases, the weight of each oxide determined separately, and the sum of their weights subtracted from the original weight of the tin dioxide. Instead of determining the amount of impurity present with the tin dioxide, the filtrate from the insoluble sulfides can be acidified with acetic acid and the tin precipitated as yellow stannic sulfide, which, after it has completely settled, can be filtered off and changed by careful ignition in an open porcelain crucible to tin dioxide, as described on p. 97, and weighed as such.

(b) Instead of igniting the precipitate, wash it into a porcelain evaporating dish, evaporate on the water bath almost to dryness, and then treat with 1 ml of pure sodium hydroxide solution and 10-15 ml of saturated sodium sulfide solution. Cover the evaporating dish with a watch glass, and heat for about 45 minutes on the water bath, whereby all the tin should pass into solution, and the other metals remain undissolved as sulfides. Filter and wash with very dilute sodium sulfide solution.

The filter upon which the metastannic acid was filtered still retains some of the precipitate. Spread it out, therefore, in a second small evaporating dish, cover with about 1 ml of sodium sulfide solution, and heat on the water bath. After half an hour, all the tin should be dissolved. Pour the solution through a small filter and wash the filter with a little hot water.

Dry the two filters, ignite in a porcelain crucible, treat the ash with a small quantity of strong nitric acid, and add the resulting solution to that obtained by dissolving the alloy in nitric acid.

For the determination of the tin, combine the two solutions containing sodium thiostannate, make acid with acetic acid, and boil to expel the hydrogen sulfide. Filter off the precipitated stannic sulfide, wash once with water to remove the most of the alkali salts, then transfer back to the original beaker and dissolve in 10 ml of 50 per cent potassium hydroxide solution and 1 g tartaric acid; these quantities suffice

for 0.1–0.2 g of tin. To the solution add pure 30 per cent hydrogen peroxide (Perhydrol, Merck) until the yellow liquid becomes perfectly colorless, then add 1 ml in excess. Boil the solution for 10 minutes to make sure that the oxidation is complete and that the excess of peroxide is decomposed. As soon as no more bubbles of oxygen are evolved, allow the solution to cool somewhat and add cautiously 15 g of oxalic acid dissolved in a little hot water. Electrolyze the hot solution as described on p. 98.

The precipitated stannic sulfide, as obtained above by acidifying the sodium thiostannate solution, may be ignited in a porcelain crucible and weighed as SnO_2. The results are usually a little high, and the method is not so accurate as the electrolytic determination. Cf. β, below.

(h) The Tin Is Present in Solution

(α) *The Solution Contains Tin Only*

If the solution contains only tin in the form of stannic salt (chloride or bromide), add a few drops of methyl orange indicator solution and then ammonia until the pink color of the indicator is changed to yellow. Add 24 g of ammonium nitrate and dilute the solution to a volume of 300 ml. Heat to boiling, filter after the precipitate has settled, wash with hot 2 per cent ammonium nitrate solution, ignite in an open porcelain crucible, and weigh as SnO_2.

Remark. If the solution contains non-volatile organic acids, this method cannot be used for the determination of tin. The tin must be first precipitated as sulfide by means of hydrogen sulfide (see below). If the tin is not in solution as stannic salt but as stannous salt, the solution must be first oxidized by the addition of bromine water until a permanent yellow color is obtained, after which the solution can be neutralized with ammonia and treated as above described.

According to J. Lowenthal,[1] tin can be precipitated from slightly *acid* stannic chloride or bromide solutions by boiling with ammonium nitrate. Add methyl orange to the solution and then ammonia until a yellow solution is obtained;[2] now add dilute nitric acid, drop by drop, until the solution just becomes pink again, and continue as described above.

(β) *The Solution Contains, besides Tin, Metals of the Ammonium Sulfide Group or Organic Substances*

In this case, irrespective of whether the tin is present in the form of stannic or stannous salts, conduct hydrogen sulfide into the dilute solution until it is saturated with the gas; allow the solution to stand until

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[1] *J. prakt. Chem.*, 56, 366 (1852).

[2] The excess of acid cannot be removed by evaporation on account of the volatility of stannic chloride.

the odor of hydrogen sulfide has almost disappeared and then filter. Wash the precipitate with a 2 per cent ammonium nitrate solution, dry, transfer as completely as possible to a porcelain crucible, and add the ash of the filter. Heat the tin sulfide at first gently with the flame well in front of the inclined open crucible to avoid loss by decrepitation, and afterwards with the flame at the base of the crucible until the odor of sulfur dioxide is no longer perceptible. Now raise the temperature gradually until finally the full heat of a good Teclu or Méker burner is obtained. As tin dioxide holds fast to some sulfuric acid with great tenacity, after cooling the crucible somewhat add a piece of ammonium carbonate the size of a pea. Again heat and weigh as SnO_2. Repeat the heating with ammonium carbonate until a constant weight is obtained.

Remark. F. Henz[1] in testing this method always obtained results which were a little too high. This was because it is difficult to wash the stannic sulfide precipitate free from sodium salts. It is best, therefore, to dissolve the well-washed stannic sulfide precipitate in a little sodium sulfide, transform the thiostannate into stannioxalate, and determine the tin by electrolysis (see below), or as oxide by the method of Löwenthal (see above directions).

2. Determination of Tin as Metal

The electrolytic deposition of tin from a solution of the ammonium stannioxalate gives excellent results It is necessary, however, to have free oxalic acid always present while the solution is undergoing electrolysis During the process, ammonium oxalate is changed by anodic oxidation into ammonium bicarbonate and carbon dioxide:

$$C_2O_4^{--} + 2H_2O - 2e = 2HCO_3^- + 2H^+$$
$$HCO_3^- + H^+ \rightleftarrows H_2O + CO_2\uparrow$$
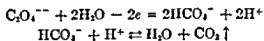
and the solution will smell of ammonia as a result of the hydrolysis of ammonium carbonate. When this point is reached no more tin is deposited. The ammonia often precipitates some stannic acid, which escapes the electrolysis. It is necessary therefore, to avoid letting the bath become ammoniacal, and this is best accomplished by adding a little solid oxalic acid from time to time.

In the following method the electrolysis is accomplished in a potassium oxalate solution. Not more than 0.3 g of tin should be present in the solution analyzed.

Procedure. In the course of an analysis it is usually necessary to precipitate the tin from a solution of alkali thiostannate. This is best accomplished as follows: Decompose the thio salt by acidifying with acetic acid, boil to expel hydrogen sulfide, and dissolve the sulfide by adding 15 g of solid potassium hydroxide. Oxidize by adding perhydrol (concentrated H_2O_2) drop by drop. At first the color of the solution

[1] Z. anorg. Chem , 37, 39 (1903).

deepens but eventually it becomes colorless. Finally boil 10 minutes, add 15 g of oxalic acid, and boil 10 minutes more. Then dilute to about 150 ml, heat to 65°, and electrolyze with a current of 1 ampere and 3-4 volts potential at the electrodes; at the end of about 6 hours all the tin will have been deposited upon a gauze electrode. Wash the deposit with water, exactly as prescribed for copper on p. 69, then with alcohol, dry, cool in a desiccator, and weigh. The results are excellent.

Remark. If ammonium oxalate is used in place of the potassium oxalate, the electrolysis requires more time (8 to 10 hours). By the addition of hydroxylamine the duration of the electrolysis is shortened.

If the solution becomes turbid during the electrolysis, insufficient caustic potash solution may be used. Add 2-3 g of potassium hydroxide to dissolve the turbidity.

Tin can also be deposited from ammonium sulfide solutions,[1] from sodium sulfide solutions,[2] and from dilute hydrochloric acid.[3] Engelenburg[4] tested the procedures of Schoch and Brown and obtained the best results as follows:

Dissolve the tin salt in 10 ml of concentrated HCl, add 2 g $NH_2OH \cdot HCl$, dilute to 200 ml, and electrolyze at 35° with a current of 1.5 amperes while stirring at 800-1000 rpm. The deposition of 0.3 g Sn is complete in 35 minutes.

Separation of Arsenic, Antimony, and Tin from the Members of the Ammonium Sulfide Group

The separation is effected by passing hydrogen sulfide into the acid solution of the above metals, whereby arsenic, antimony, and tin are precipitated as sulfides while the remaining metals remain in solution.

From an alloy, or the solid sulfo salts of the above metals, arsenic, antimony, and tin may be readily volatilized by heating in a stream of chlorine; the chlorides of these three metals are readily volatile, whereas those of the remaining metals are only difficultly so.

Separation of Arsenic, Antimony, and Tin from Mercury, Lead, Copper, Cadmium, and Bismuth

The qualitative analysis of a mixed sulfide precipitate containing the above metals has been described in Vol I ("Analysis of Group II"). As a result of treatment with Na_2S_2 or $(NH_4)_2S_2$, the sulfides of As, Sb, and Sn pass into solution, together with Hg if Na_2S_2 is used, Cu, Pb, Bi, and Cd sulfides remaining undissolved. If $(NH_4)_2S_2$ is used, Hg is included in the Cu group.

[1] Classen, Quan. Anal. durch Elektrolyse; Medway, Am. J. Sci., [4] 18, 56, 180 (1904); Exner, J. Am. Chem. Soc., 25, 896 (1903); Fischer and Boddaert, Z. Elektrochem., 10, 945 (1904); Witmer, J. Am. Chem. Soc., 29, 473 (1907); Smith and Kollock, J. Am. Chem. Soc., 27, 1527 (1904).
[2] W. D. Treadwell, Elektroanalyt. Methoden.
[3] Schoch and Brown, J. Am. Chem. Soc., 38, 1660 (1916).
[4] Z. anal. Chem., 62, 257 (1923).

This procedure, though satisfactory from a qualitative point of view, does not effect a complete separation of the eight elements, and the quantitative analysis of a sulfide precipitate containing them all is a very complex problem. No simple process of general applicability can be given. The chief difficulties are:

1. Generally speaking, slightly incomplete extraction of tin and antimony from the mixed precipitate, necessitating a repetition of the procedure.

2. Partial solubility of copper and bismuth sulfides in alkaline polysulfides.

3. Insolubility of stannous sulfide in alkaline monosulfide, and incomplete extraction of antimony bisulfide by that reagent.

4. In the presence of mercury, formation of mixed or complex sulfides of mercury with cadmium, tin, or copper, which modifies the reactions of these metals.

However, the simultaneous presence of all the above metals in one and the same substance is so rare an occurrence that it may be ruled out for practical purposes. In particular, mercury is not abundant in nature and is seldom found in alloys; its principal ore, cinnabar, may be found associated with sulfides of Fe, Cu, As, Sb, and Pb. The mercury determination in such ores is usually accomplished by a volatilization process (cf. p 56). In Eschka's method, the powdered ore is mixed with pure iron filings in a tall porcelain crucible supported by a well-fitting perforated asbestos plate so that only the lower third of the crucible projects below the plate. The crucible is closed with a tight-fitting concave gold lid filled with water. The bottom of the crucible is heated by a small flame. After cooling, the lid is removed, washed with alcohol, dried for a very short time, and weighed. The lid is then gently ignited and again weighed, the difference giving the mercury.

Cadmium is another element which is rarely met with in minerals other than zinc ores, in which it occurs in small quantities. It is an important constituent of certain fusible alloys: thus, Wood's metal consists of Bi, Cd, Sn, and Pb. Its analysis is conducted like that of tin alloys (p. 94), the tin being separated as insoluble metastannic acid by treatment of the alloy with nitric acid. The nitrates of the other metals are converted into chlorides, and the lead chloride can be collected as a residue insoluble in alcohol. Bismuth is then precipitated as oxychloride (p. 63), the cadmium is left in solution, from which it is recovered as sulfide, and this is converted into and weighed as sulfate (p 71).

The metals other than mercury and cadmium are more frequently found together, and their separation will now be considered.

Separation of Arsenic, Antimony, and Tin from Lead, Bismuth, and Copper

The separation is carried out, as in qualitative analysis, by treatment with alkaline sulfide, forming soluble thio salts of As, Sb, and Sn and insoluble sulfides of Pb, Cu, and Bi. It is generally preferable to use sodium sulfide; if Sb preponderates, potassium sulfide should be used, as the sodium salt of complex Sb salts is sparingly soluble; ammonium sulfide is used in separations affecting mercury.

The best separation is obtained if all the metals are in solution (case a); if they are in the form of a sulfide precipitate, the separation to be quantitative may have to be repeated (case b). If the metals are present as an alloy, low-temperature fusion with sodium sulfide is very convenient and effective (case c). Lastly, if insoluble or complex compounds have to be treated, fusion with sodium carbonate and sulfur is recommended (case d).

(a) **The Metals Are in Solution.** The metals should be in their higher state of oxidation (solution in *aqua regia*, or chloride solution treated with potassium chlorate or nitric acid). Add at least six times as much tartaric acid as there are metals present, and a slight excess of sodium hydroxide. Dilute to about 100 ml, pour the hot solution drop by drop, while stirring, into a hot solution of 5 to 10 g of sodium sulfide in 100 ml of water. Digest on the water bath for half an hour, pass hydrogen sulfide through the liquid, allow the precipitate to settle, filter, and wash the precipitate thoroughly with dilute sodium sulfide solution.

(b) **The Metals Are Contained in a Sulfide Precipitate.** Heat the precipitate with a solution of 5 to 10 g of sodium sulfide in less than 50 ml of water. After boiling for a minute, allow the precipitate to settle on the water bath, and if it shows a yellow color, treat with sodium sulfite solution (p. 94), stir, dilute with 100 ml of hot water, and set aside on the water bath for half an hour. Filter off the precipitate and wash it with dilute sodium sulfide solution. Unless it is quite small, it is advisable always to retreat the precipitate, by dissolving it in aqua regia and applying procedure (a). Combine the filtrates (containing As, Sb, Sn).

(c) **The Metals Occur as an Alloy.** White alloys (lead or tin base bearing metals) and copper alloys are most commonly met. In the case of white alloys, oxidize 1 g of drillings with nitric acid in a porcelain dish, and evaporate to dryness. Triturate the residue with a flattened glass rod, mix with 10 g of sodium sulfide crystals and 0.2 g of powdered sulfur, and gently heat the covered dish so that the salt melts in its water of crystallization. Continue the digestion for half an hour; dissolve the product in 100 ml of hot ammonium nitrate solution. After another hour's digestion, collect the precipitate and wash it with dilute sodium sulfide solution. The filtrate contains all the tin and antimony (arsenic); the residual lead sulfide is free from these metals.[1]

In the case of copper alloys, separate the tin and antimony from the remaining metals by treating the alloy with nitric acid (see " Analysis of Phosphor Bronze," p. 101). The tin is left behind as metastannic acid, insoluble in dilute nitric acid, and the antimony is precipitated completely if ten times as much tin is present. In the presence of sufficient tin, all phosphorus and arsenic are also found in the insoluble residue as P_2O_5 and As_2O_5. A small quantity of arsenic (and the remaining metals of this group) can be precipitated by hydrogen sulfide and separated from the copper group by means of alkaline sulfide solution (see b).

[1] Biltz, *Z. anal. Chem.*, **81**, 81 (1930).

(d) **The Metals Occur as Insoluble Compounds.** Fuse the substance with 6 parts of sodium carbonate and sulfur mixture, etc., as directed on p. 94.

For the determination of antimony in lead sulfate, etc., dissolve the lead salt in excess of potassium hydroxide, and pour the liquid into hot potassium sulfide solution (see *a*).

ANALYSIS OF PHOSPHOR BRONZE

Standard Sample 63 of the National Bureau of Standards contains, in addition to copper, tin, lead, and phosphorus, 0.55 per cent of antimony, 0.48 per cent of zinc, 0.27 per cent of iron, 0.20 per cent of arsenic, 0.05 per cent of sulfur, 0.05 per cent of aluminum, and 0.008 per cent of nickel. In the procedure to be described only the first four elements will be considered. In this procedure, the antimony will be determined with the tin in a precipitate of "metastannic acid" and will be counted as tin. The arsenic will also be present in this precipitate as As_2O_5.

Determination of Copper and Lead

Procedure. Dissolve 0.5 g of borings in a small beaker with 15 ml of 6 N nitric acid, *d* 1.2. Evaporate the solution just to dryness on the water bath, and remove the beaker as soon as this stage is reached. Treat the residue with 20 ml of 2 N nitric acid, heat to boiling, and decant off the solution through a hardened filter paper. Repeat this treatment. Complete the washing by boiling and decanting with 1 per cent ammonium nitrate solution. Keep as much of the precipitate as possible in the original beaker, and the total volume of the filtrate under 150 ml. Examine the first portions of the filtrate for metastannic acid, refilter if necessary, and remove each successive portion from below the funnel before adding more wash water. Wash the precipitate with 1 per cent NH_4NO_3 solution until a portion of the filtrate will give no test for copper or lead on adding a little ammonium sulfide solution (or for copper with $K_4Fe(CN)_6$ solution). Save the precipitate for the tin determination.

To determine the copper and lead electrolyze this solution, and the nitric acid solution obtained below, with platinum gauze electrodes; use a current of 0.25 ampere for 4 to 6 hours and then one of 0.1 ampere for 18 to 20 hours. The copper will be deposited on the cathode as metallic copper and the lead upon the anode as PbO_2. (See p. 75.)

Determination of Tin

With the aid of a stream of water from a wash bottle, transfer the insoluble residue back to the original beaker as completely as possible

but limit the quantity of water used as far as practicable. To dissolve the precipitate remaining on the filter, spread it out on the bottom of a beaker, pour over it 25 ml of yellow ammonium sulfide solution, and heat gently for 15 minutes. Meanwhile add 75 ml of the sulfide solution to the residue in the original beaker. Add to this the ammonium sulfide solution from the treatment of the filter paper, and wash the paper 3 times with hot water. Save the filter paper.

Cover the beaker containing the ammonium sulfide solution with a watch glass and digest at 60° to 70° for 2 hours. Then filter off any black residue and collect the filtrate in a 600-ml beaker. Wash the residue with 100 ml of ammonium sulfide reagent which has been diluted with 4 times as much water. Complete the washing with water. Treat this filter and the one previously saved with 15 ml of hot 3 N HNO$_3$, filter, wash free from acid with hot water, and add this solution, after nearly neutralizing it with ammonia, to that in which the copper and lead is to be determined (see above). Add the residue to the Sn precipitate.

To the ammonium sulfide solution add acetic acid until the solution reacts acid, and allow to stand in a warm place for at least 3 hours. Then filter off the SnS$_2$ precipitate and wash it with 2 per cent NH$_4$NO$_3$ solution, using at least 150 ml of it. Transfer the moist SnS$_2$ precipitate to a weighed porcelain crucible and ignite carefully. Call the residue SnO$_2$, and report the percentage of tin present in the alloy.

Determination of Phosphorus[1]

Weigh out 1–3 g of sample into a 300-ml Erlenmeyer flask and dissolve in 20 ml of aqua regia. When all the metal has dissolved add 10 ml of water and digest at 90° for 10 minutes. Dilute to 50 ml and treat with 100 ml of ammonium molybdate solution prepared as recommended by Blair (see Chapter IX).

Stopper the flask with a rubber stopper and shake for 10 minutes, occasionally removing the stopper. Allow to stand 4 hours or longer before filtering. Filter, keeping as much as possible of the precipitate in the flask. Wash the precipitate 5 times by decantation with 10-ml portions of 1 per cent nitric acid.

Dissolve the precipitate on the filter in 5 N ammonium hydroxide containing 0.5 g of citric acid. Pour this on the filter in small portions, and catch the filtrate in the original flask containing the bulk of the precipitate. Do not use more than 50 ml of the ammonium hydroxide. Warm the solution slightly to dissolve the precipitate, replace under

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[1] Method of Lundell and Hoffman, *Ind. Eng. Chem.*, **15**, 172 (1923).

the funnel, and wash the filter with a little hot 5 per cent hydrochloric acid. If the ammoniacal filtrate is not clear at this stage, filter through the same filter and wash the filter with hot water.

Make the solution acid with hydrochloric acid, and, without regard to a slight precipitate of molybdic acid, which, however, seldom forms in the analysis of alloys with low phosphorus, add 20 ml of magnesia mixture (Chapter IX). Heat to boiling and slowly add ammonium hydroxide till a precipitate forms or the solution is ammoniacal. Finally add enough 15 N ammonium hydroxide to make the solution 1.5 N with ammonia and allow to stand 4 hours. Filter, wash with cold 1.5 N ammonium hydroxide, and finish the analysis as described under "Phosphoric Acid" in Chapter IX.

ANALYSIS OF BABBITT'S METAL

The National Bureau of Standards distributes two standard alloys: one containing about 79 per cent lead, 11 per cent tin, and 10 per cent antimony; and another containing about 88.3 per cent tin, 7.3 per cent antimony, 3.8 per cent copper, and 0.6 per cent lead. The alloys contain traces of iron, bismuth, and arsenic which need not concern us here.

Determination of Lead

Take samples of about 0.4 g, weighed carefully to four significant figures. Treat each sample in a 250-ml Erlenmeyer flask with 25 ml of a saturated solution of bromine in concentrated hydrochloric acid. After a few minutes, heat gently but take care not to boil off all the bromine until the alloy is entirely decomposed. Pay no attention to the formation of a white precipitate of lead chloride. When none of the original alloy remains, heat to expel the excess bromine; the solution will become colorless or pale yellow in color. Remove from the heat and cool somewhat. Add 15 ml of 18 N H_2SO_4 (concentrated acid added carefully to an equal volume of water) and evaporate until dense fumes of sulfuric acid are evolved and all HCl is expelled. Cool, dilute to about 100 ml, and allow to stand at least an hour. Filter through a Gooch crucible that has been washed with alcohol and with ether and weighed after heating to about 400° (see p. 58). Wash the precipitate under gentle suction with six 5-ml portions of 1.8 N H_2SO_4 and then with six portions of alcohol and finally four portions of ether. Dry the crucible at 105° for about 15 minutes, and then heat strongly inside a large crucible; cool in a desiccator and weigh. From the weight of this lead sulfate calculate the percentage of lead in the alloy.

Sometimes the results are high because some undissolved alloy remains with the lead sulfate. To recover this, wash the weighed $PbSO_4$ repeatedly with hot $2 N$ $NH_4C_2H_3O_2$ until the washings give no test with K_2CrO_4 solution; heat as before, cool, and weigh. Deduct the weight of residue from that of the impure precipitate and make a corresponding correction in the antimony determination.

Determination of Antimony

Digest accurately weighed 0.4-g samples of alloy in 250-ml flasks with 12 ml of concentrated H_2SO_4 and about 5 g of $KHSO_4$. Heat over a free flame while constantly rotating the contents of the flask until all the metal has dissolved and the contents of the flask fume strongly.

It is desired to get the antimony into solution as $Sb_2(SO_4)_3$ and the tin as $Sn(SO_4)_2$.

$$2Sb + 6H_2SO_4 = Sb_2(SO_4)_3 + 3SO_2 + 6H_2O$$
$$Sn + 4H_2SO_4 = Sn(SO_4)_2 + 2SO_2 + 4H_2O$$
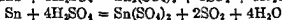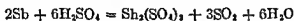
If the alloy is heated too gently, sometimes a part of the tin is left in the stannous condition, and this is fatal to the analysis. The acid should be heated nearly to the boiling point to accomplish the second stage in the oxidation of the tin. A black residue of finely divided antimony often requires prolonged heating.

When the sample is completely decomposed and the sulfuric acid has fumed strongly for several minutes, allow to cool and then add very cautiously 5 ml of water. Follow this with 20 ml of $12 N$ hydrochloric acid and boil gently for 3 minutes. Cool, add 100 ml of cold water, and titrate at a temperature below 15° with 0.1 N permanganate. The end point should remain for 20 seconds if the above directions were followed. Save the solution for the tin determination.

According to Lundell,[1] the solution should contain 10 to 25 per cent of concentrated HCl by volume, and approximately 10 per cent by volume of concentrated H_2SO_4 is desirable. These directions provide for 10 per cent of HCl and somewhat less than 6 per cent of H_2SO_4 by volume. The procedures recommended by the Bureau of Standards and by Lundell, Hoffman, and Bright call for less than 5 per cent H_2SO_4. The titration of antimony with permanganate gives very accurate results when the conditions are right, and this method of determining antimony is used more than any other in commercial testing. If the conditions are not right, the end point may be very hard to find. For many years chemists avoided as much as possible all titrations with permanganate in the presence of hydrochloric acid because hydrochloric acid is easily oxidized to chlorine or hypochlorous acid, a reaction which is catalyzed by the presence of other substances such as ferrous salt. By keeping the solution cold, by making sure that all tin, iron, etc., are oxidized by sufficiently long treatment with hot sulfuric acid, and by adding appropriate quantities of hydrochloric and sulfuric acids, this oxidation of HCl is prevented. The titration reaction can be expressed as follows:

$$5Sb^{+++} + 2MnO_4^- + 12H_2O = 5H_3SbO_4 + 2Mn^{++} + 9H^+$$
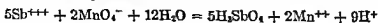
and the milliequivalent of antimony is 0.06088 g.

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[1] *Applied Inorganic Analysis*, p. 228.

Determination of Tin

Transfer the titrated solution from the antimony determination to a 500-ml Erlenmeyer flask; add 65 ml more of concentrated hydrochloric acid and about 2 g of test lead powder. Stopper the flask with a rubber stopper carrying a long glass tube which extends from the bottom of the stopper upward for about an inch and then bends downward through a wide arc to a point on the outside nearly level with the bottom of the flask when the stopper is inserted. Heat the contents of the flask to boiling and boil gently for 30 minutes. Then remove the flame and, without removing the stopper from the flask, insert the outer end of the tubing it carries into a beaker containing 200 ml of saturated NaHCO₃ solution (about 22 g of NaHCO₃). While keeping the tubing in this NaHCO₃ solution, cool the contents of the flask by cold, running water. Cool slowly at first. At the end of the reduction with lead,

$$Sn^{++++} + Pb = Sn^{++} + Pb^{++}$$

the flask is filled with steam; but as the contents cool and the steam condenses, the NaHCO₃ solution is sucked into the flask and CO₂ is formed which exerts a pressure and will force back the liquid in the tubing and perhaps bubble through the NaHCO₃ solution. In this way the flask becomes filled with CO₂ rather than air, of which the oxygen would oxidize some of the stannous ions back to the stannic state. Finally cool to about 10° (using ice water or Dry Ice if necessary), add 5 ml of starch indicator solution, and titrate fairly rapidly with 0.1 N iodine solution.

$$Sn^{++} + I_2 = Sn^{++++} + 2I^-$$
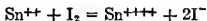
Instead of using the above device for filling the flask with CO₂, a stream of CO₂ gas can be kept passing through the solution during the reduction with Pb and particularly during the cooling of the solution. Some chemists add a lump or two of calcite (CaCO₃) to the reduced solution which slowly dissolves in the acid with liberation of CO₂. A little Dry Ice placed in another flask will furnish a convenient source of CO₂. On placing this flask in warm water, an abundant stream of CO₂ is evolved which can be led into the flask containing the solution of the alloy by means of tubing extending nearly to the bottom of the flask containing the solution that is being analyzed. The above scheme of sucking NaHCO₃ back into the solution works nearly as well. It has been recommended that the iodine solution be added through tubing that runs through the stopper so that there is absolutely no chance for air to enter the flask during the titration. The titration of SnCl₂ with iodine is very accurate, but it is necessary to have all the tin in the stannous condition and to prevent any back oxidation by air, or the results of the analysis will be low. Various other reducing agents such as a coil of nickel wire, metallic iron, or powdered antimony have been recommended instead of the test lead, but in every case the chief source of trouble is oxidation by the air.

GERMANIUM, Ge. At. Wt. 72.60

Forms: GeO₂, Mg₂GeO₄

Germanium is a very rare element which resembles tin. In ordinary mineral analysis, practically all the germanium will be lost by volatilization as GeCl₄ during evaporation with HCl before removing the silicic acid. This volatility of GeCl₄ is utilized for separating germanium from other elements. With a suitable distilling column, germanium can be separated not only from elements that do not form volatile chlorides but also from elements such as arsenic, tin, antimony, tellurium, and selenium that do.[1] Germanium minerals are decomposed best by fusion with 6 times as much of a mixture of equal parts sodium carbonate and sulfur in a covered porcelain crucible. In this way water-soluble Na₂GeS₃ is formed. To make sure that a perfect separation is obtained, the melt is leached with water, filtered, and the fusion of the insoluble residue with sodium carbonate and sulfur repeated. The combined aqueous extracts of the melts are made strongly acid with H₂SO₄ and the precipitated GeS₂, SnS₂, As₂S₃, etc., filtered off. When no other element of this group is present, the white GeS₂ can be converted into (a) GeO₂ or (b) Mg₂GeO₄ as follows:

(a) Dissolve the white GeS₂ in small portions of strong ammonia solution and catch the solution in a weighed platinum dish or large crucible. Wash the filter with small portions of water until the filtrate is colorless. Add 20 ml of 3 per cent H₂O₂ and allow the oxidation to take place in the cold. Evaporate the solution to dryness and heat to 105°. Moisten the residue with H₂SO₄ and heat carefully over a free flame and finally to constant weight at 900°. Weigh as GeO₂.

(b) Dissolve the GeS₂ precipitate in ammonia as in (a) and oxidize with H₂O₂. Heat until all excess peroxide is removed. Make slightly acidic with H₂SO₄, dilute to 100 ml, and add 20–25 ml of 2 N (NH₄)₂SO₄ solution and 15–25 ml of N MgSO₄ solution. Add strong ammonia slowly until an excess of 15–20 ml has been added for each 100 ml of solution. Allow to stand over night, filter, and wash with small portions of 1.5 N NH₄OH. Ignite in a porcelain crucible, as with magnesium ammonium phosphate (see "Magnesium"), and weigh as Mg₂GeO₄.

To determine germanium in germaniferous zinc oxide, proceed as follows:

Take 20–100 g of oxide, triturate to a paste with water, and transfer to a flask containing NaOH solution. A proper mixture is 1 part NaOH, 2 parts crude zinc oxide, and 5 parts water. Provide the flask with a three-holed rubber stopper carrying gas inlet tubing which reaches to the bottom of the flask, a small dropping funnel, and a small distilling column, 20 mm in diameter and 80 cm long, filled with glass beads and surrounded by a glass jacket tube. To the end of the distilling column attach a Liebig condenser, and to the other end of the condenser attach an adapter which passes through a two-holed rubber stopper to the bottom of a small Erlenmeyer flask. Connect this flask with a second flask by means of tubing which reaches from the bottom of the stopper of the first receiver to the bottom of the second flask. Add water to each flask sufficient to cover the inlet tubes, and immerse the flasks in ice water. Also immerse the distilling flask in cracked ice, fill the apparatus with chlorine, and slowly add concentrated HCl through the dropping funnel until all the NaOH is neutralized and then excess HCl equal to twice the

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[1] Dennis and Papish, *J. Am. Chem. Soc.*, **43**, 2140 (1921); James and Fogg, *ibid.*, **51**, 1459 (1929); Dennis and Johnson, *ibid.*, **45**, 1380 (1923); Johnson and Dennis, *ibid.*, **47**, 790 (1925).

weight of zinc oxide. Remove the ice and heat gently. Distil until half the liquid in the flask is gone, add an equal volume of concentrated HCl, and distil again. Repeat this a third time. Finally saturate the contents of the two Erlenmeyer flasks with H_2S and allow to stand 24 hours. Filter off the GeS_2 and analyze as above.

As_2S_3 and GeS_2 can be separated by dissolving them in ammonia, adding a liberal quantity of HF in a platinum dish, and precipitating the arsenic with H_2S. The HF converts the germanium to H_2GeF_6, and the GeF_6^{--} anion does not react with H_2S (cf. Vol. I).

SELENIUM, Se. At. Wt. 78.96

Selenium is usually determined as the element itself. Two cases are to be considered:

(a) The selenium is present as alkali selenite or as H_2SeO_3.

(b) The selenium is present as alkali selenate or as H_2SeO_4.

(a) **The Selenium Is Present as Selenite or as Free H_2SeO_3.** Make the solution acid with HCl, saturate with SO_2 gas, boil, filter through a Gooch crucible, and wash, first with water then with alcohol. Dry the residue at 105° and weigh.

Remark. The precipitation of selenium by SO_2 is quantitative whether the solution is concentrated or dilute, but it takes place more readily in the presence of considerable acid. This fact is of importance in the separation of selenium from tellurium, for the latter element is not precipitated by SO_2 when considerable hydrochloric acid is present (cf. p. 108).

In the presence of nitric acid the precipitation of selenium by sulfurous acid is incomplete. In such cases, the nitric acid may be removed by boiling with hydrochloric acid in a flask with a return-flow condenser. Evaporation in an open vessel is not permissible as considerable selenium is volatilized even in the presence of dissolved alkali chloride. It is safer to precipitate the selenium with hydrazine sulfate or hydrazine hydrate when nitric acid is present.

Add ammonium hydroxide to the nitric acid solution until it is faintly ammoniacal and then make slightly acid with hydrochloric acid. Cover the Erlenmeyer flask with a watch glass, add an excess of hydrazine sulfate or hydrate, and boil until the precipitated red selenium coagulates and changes into the easily filtrable gray modification with a clear supernatant solution. Filter into a Gooch or Munroe crucible, wash with hot water and then with alcohol, dry at 105°, and weigh the selenium.

Phosphorous acid does not precipitate selenium from cold, dilute, strongly acid solutions; this fact is utilized in the separation of selenium from mercury (cf. p. 111).

(h) **The Selenium Is Present as Alkali Selenate or as Free H_2SeO_4.** As selenium in the form of selenic acid is not precipitated by sulfur dioxide, phosphorous acid, or hydrogen sulfide, it must be first reduced to selenious acid by long-continued boiling with hydrochloric acid (cf. Vol. I); the above procedure is then followed. This tedious operation is unnecessary, however, if the precipitation is effected with hydrazine hydrate or sulfate as described under (a).

In practice, selenium is obtained usually in neither of the above forms, but as impure selenium (selenium sponge) or as selenide, and by the treatment of these substances one or the other of the above selenium compounds is obtained.

If the selenium or selenide is made to react with concentrated nitric acid,[1] or aqua regia, all of it is dissolved in the form of selenious acid (not selenic acid), and the selenium can be precipitated with hydrazine hydrate or sulfate as described under (a).

If the finely powdered selenium or selenide is intimately mixed with 2 parts sodium carbonate and 1 part potassium nitrate, placed in a nickel crucible, covered with a layer of sodium carbonate and potassium nitrate, and heated gradually until it fuses, all the selenium forms alkali selenate and on extracting the melt with water it goes into solution; in this way it is separated from most of the remaining oxides. The solution, however, often contains small amounts of lead. In order to remove lead, treat the filtrate with hydrogen sulfide, and again filter; free the solution from hydrogen sulfide by boiling, strongly acidify with hydrochloric acid, boil until no more chlorine is evolved, and precipitate the selenium by sulfur dioxide according to (a).

Remark. The mixture must be heated very slowly, as otherwise some selenium is likely to be lost by volatilization. In working with selenium it must be borne in mind that selenium is easily volatilized as $SeO_2 \cdot 2HCl$. If the solution is less than 6 N in HCl it can be heated on the steam bath without serious loss, but when stronger acid is used and the solution is evaporated to dryness on the steam bath, a very serious loss results. Alkali salts do not prevent volatilization, and volatile Se_2Cl_2 is easily formed in strong HCl solutions containing reducing agents or filter-paper fiber. In ordinary work when no provision is made for selenium or tellurium, they are likely to be reported as aluminum. If any considerable quantity of either were present it would be revealed in reductions incidental to the determination of iron.

TELLURIUM, Te.   At. Wt. 127.6

Tellurium is usually determined as the element itself.

If sulfur dioxide is conducted into a hydrochloric acid solution containing tellurous acid, black tellurium is precipitated quantitatively,

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[1] Mercury selenide is not acted upon by nitric acid, but is dissolved by aqua regia.

provided that the solution does not contain too much acid. If tellurous acid is dissolved in 200 ml of concentrated hydrochloric acid, no tellurium will be precipitated on passing sulfur dioxide into the cold solution. If, however, the solution is diluted with an equal volume of water and sulfur dioxide is passed into the boiling solution, all the tellurium will be precipitated. Filter off the precipitate, wash with water until free from chlorides, then with alcohol, dry at 105°, and weigh. The oxidation of the tellurium during the drying is so slight that it can be disregarded.

From solutions of telluric acid, tellurium is not precipitated by means of sulfur dioxide. From such solutions the precipitation can be accomplished by boiling for a long time under a return-flow condenser with strong hydrochloric acid which reduces telluric acid. According to Gutbier, this reduction is unnecessary if hydrazine hydrochloride or hydrate is used to precipitate the tellurium.

$$2H_4TeO_6 + 3(N_2H_4 \cdot 2HCl) = 12H_2O + 6HCl + 3N_2 + 2Te$$
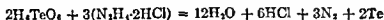
Lenher and Homberger prefer to use both hydrazine hydrochloride and sulfurous acid. Their procedure is as follows: To the solution of tellurite, tellurate, or the corresponding acids, containing about 0.5 g of tellurium, add 25 ml of 3 N hydrochloric acid, 10 ml of a 15 per cent solution of hydrazine hydrochloride, and 35 ml of saturated sulfur dioxide solution. Boil 5 minutes, filter, wash with hot water till free from chloride, then with alcohol, dry at 105°, and weigh as tellurium. The entire analysis can be made in an hour.

Separation of Selenium and Tellurium from the Metals of Groups III, IV, and V

By conducting sulfur dioxide into the solution fairly acid with hydrochloric acid, the selenium and tellurium will be quantitatively precipitated while the other metals remain in solution.

Separation of Selenium and Tellurium from the Metals of Group II

(a) From Copper, Bismuth, and Cadmium

Pass sulfur dioxide into the boiling solution containing hydrochloric acid, whereby all the selenium and tellurium and usually some of the bismuth are precipitated. Filter and wash the precipitate with hot water. Dissolve it in nitric acid, evaporate the solution to dryness, take up in concentrated hydrochloric acid, dilute with a little water, and precipitate with hydrogen sulfide. Wash the precipitate, consisting of the sulfides of selenium, tellurium, and bismuth, and treat with sodium sulfide solution; selenium and tellurium pass into solution while the bismuth remains behind as its brown sulfide and is filtered off.

Make the solution containing the selenium and tellurium acid with nitric acid, carefully evaporate to dryness, and boil the residue with

200 ml of concentrated hydrochloric acid, until there is no longer any evolution of chlorine. Filter off the deposited sulfur through a Gooch crucible, and saturate the filtrate with sulfur dioxide gas; all the selenium is precipitated in this way. Filter off the selenium through a Gooch crucible and wash successively with 10 N, 6 N, and 2 N hydrochloric acid, and finally with absolute alcohol. Dry the precipitate at 105° and weigh. Dilute the filtrate with an equal volume of water and precipitate the tellurium by passing sulfur dioxide into the boiling solution. Wash this precipitate with water until free from chlorides, then with absolute alcohol, dry at 105°, and weigh.

Remark. The above method is suitable for the separation of selenium and tellurium from small amounts of bismuth, but does not effect a good separation of selenium (and tellurium) from copper. In this case, more or less copper selenide is formed according to the conditions, and this compound is not decomposed quantitatively by sodium sulfide.[1] The following method of B. Brauner and B. Kuzma[2] is more satisfactory.

Precipitate the tellurium and selenium in a pressure flask, by means of SO_2, filter off the precipitate, which is contaminated with copper, antimony, and bismuth (using a Gooch crucible), wash, dissolve in nitric acid, evaporate the solution to dryness, and take up the residue in caustic potash solution (1 : 5). To the alkaline solution in an Erlenmeyer flask upon a water bath, add little by little 4–6 g of ammonium persulfate, whereby the potassium tellurite is oxidized to potassium tellurate and the selenite to selenate. When all the persulfate has been added, boil the solution to decompose the excess of persulfate, make acid with sulfuric acid, and allow to cool. Now, add 100 ml of H_2S-water, expel the excess of the H_2S by passing CO_2 through the solution, filter off the precipitated CuS (Bi_2S_3, Sb_2S_3), and treat as described on pp. 78–81. Boil the filtrate with hydrochloric acid to reduce the telluric acid to tellurous acid, reduce the solution by SO_2, and analyze as described above.

The first filtrate from the impure Te and Se will contain the greater part of the Cu, Bi, etc.

(b) From Antimony, Tin, and Arsenic

If considerable antimony is present, add tartaric acid to the solution, and precipitate the selenium and tellurium by boiling with sulfur dioxide.

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[1] Cf. E. Keller, *J. Am. Chem. Soc.*, **19**, 771.

[2] Ber., 1907, 3362.

According to Muthmann and Schröder[1] this method of separating tellurium from antimony is not **quantitative**; some antimony is always precipitated with the tellurium. A. Gutbier,[2] however, finds that a perfect separation can be accomplished by means of hydrazine hydrochloride (not the sulfate).

(c) From Mercury

Dissolve the mercury selenide, or telluride, in aqua regia, add chlorine water, and dilute the solution largely with water. Add phosphorous acid;[3] after 24 hours' standing, the mercury is precipitated completely as mercurous chloride, and can be determined as such according to p. 55. Make the filtrate slightly alkaline with potassium hydroxide, evaporate nearly to dryness, dilute, and separate the selenium from the tellurium according to the method of Keller (see below).

(d) From Gold and Silver

The separation of selenium and tellurium from silver offers no difficulty, inasmuch as the silver can be precipitated by hydrochloric acid and determined as the chloride.

Precipitate the gold as described on p. 128 by oxalic acid and the selenium and tellurium in the filtrate by means of sulfur dioxide. The three metals may also be precipitated together by sulfur dioxide, weighed, and the selenium and tellurium afterward volatilized by roasting, leaving the gold behind.

Tellurium may be separated from gold by precipitating the gold with ferrous sulfate. Selenium, however, is also precipitated quantitatively by ferrous sulfate from solutions strongly acid with hydrochloric acid.

Separation of Selenium from Tellurium

Method of E. Keller[4]

Keller's method is based upon the fact that tellurous acid is not precipitated from solutions strongly acid with hydrochloric acid while selenium is precipitated quantitatively.

Procedure. Dissolve the mixture of the two elements, obtained by precipitation with sulfur dioxide, in nitric acid and carefully evaporate

[1] Z. anorg. Chem., 14, 433 (1897).
[2] Z. anorg. Chem., 32, 263 (1902).
[3] Selenious and tellurous acids are not precipitated by phosphorous acid from dilute hydrochloric acid solution, but are precipitated from hot concentrated solutions.
[4] J. Am. Chem. Soc., 19, 771.

to dryness. Treat the dry mass with 200 ml of concentrated hydrochloric acid, boil to remove the nitric acid, and saturate with sulfur dioxide. Filter off the precipitated selenium through a Gooch crucible, wash first with 10.8 N hydrochloric acid, then with dilute hydrochloric acid, then with water until free from chloride, and finally with absolute alcohol. Dry the selenium at 105° and weigh. Dilute the filtrate with an equal volume of water, heat to boiling, precipitate the tellurium by sulfur dioxide, and treat like the selenium.

According to Keller, this method gives satisfactory results as long as the amount of tellurium present does not exceed 5 g. Even then the separation can be effected by increasing the amount of acid to 450 ml.

Determination of Selenium and Tellurium in Crude Copper

Many copper ores contain selenium and tellurium, and the crude copper obtained from such ores always contains these elements. The amount present may be determined, according to Keller,[1] as follows: According to the amounts of selenium and tellurium present, take 5–100 g of the copper for analysis. Dissolve the sample in nitric acid, and add an excess of ammonia to precipitate the phosphorus, arsenic, antimony, tin, bismuth, selenium, and tellurium together with ferric hydroxide;[2] the copper is held in solution by the excess of ammonia. Filter off the precipitate and wash with dilute ammonia water until the copper is completely removed. Dissolve the precipitate in hydrochloric acid and saturate this solution with hydrogen sulfide in the cold; selenium and tellurium together with arsenic, antimony, tin, and bismuth are thrown down as sulfides and are separated by filtration from the iron and phosphorus. Treat the precipitate thus obtained with sodium sulfide solution, and filter. The filtrate contains all the selenium and tellurium in the presence of arsenic, antimony, and tin as thio salts. Make acid with nitric acid and carefully evaporate to dryness. Dissolve the residue in 200 ml of concentrated hydrochloric acid and treat as described on p. 111.

Determination of Selenium in Steel[3]

Cover 25 g of steel with 125 ml of water and gradually add 130 g of pure iodine while stirring. This dissolves the metal and any tellurium present but leaves a residue of oxides, selenides, and elementary selenium.

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[1] *J. Am. Chem. Soc.*, 22, 241.

[2] About 0.2 g of ferric iron should be present. If necessary, add some iron dissolved in nitric acid.

[3] Methods of the Chemists of the U. S. Steel Corporation.

Filter and wash with 10 per cent KI solution until all FeI$_3$ is removed and then a few times with water to remove KI. Place the filter paper and precipitate in the flask of an all-glass Soxhlet extraction apparatus in which the thimble is omitted and the thimble compartment is filled with glass beads. Add 20 ml of 70 per cent HClO$_4$ to the flask and heat gently until the filter paper is destroyed. When condensate appears in the thimble compartment and the HClO$_4$ is fuming strongly, cool somewhat, disconnect the Soxhlet condenser, and rinse the connections into the flask. Then rinse the condenser with concentrated HCl which flows into the thimble compartment; disconnect the condenser, and rinse it and the connections with a little water. Finally pour concentrated HCl over the beads until enough is present to start the automatic siphon and make the washings run into the flask. The volume of the entire solution should not exceed 90 ml at this point.

Filter through a glass or Alundum crucible and wash with 10–15 ml of concentrated HCl. Add 50 ml of concentrated HCl which has been freshly saturated with SO$_2$. Allow to stand until the red selenium settles, filter through a Gooch crucible, and wash with cold, concentrated HCl and finally with water until free from chloride. Wash 4 times with 5-ml portions of alcohol and 4 times with ether, drain 5 minutes with suction and 15 minutes at 100°. Cool and weigh as Se.

MOLYBDENUM, Mo. At. Wt. 95.95

Forms: MoO$_3$, PbMoO$_4$

If the molybdenum is present as ammonium molybdate, heat a weighed portion in a spacious porcelain or platinum crucible, at first carefully and later to a dull red heat; this leaves the molybdenum trioxide behind in the form of a dense powder, appearing yellow when hot and almost white when cold. There is no danger of losing any of the molybdenum by volatilization, provided that the dull red heat is not exceeded.

If the molybdenum is present as alkali molybdate, change it to mercurous molybdate or to its sulfide, and then analyze as described below.

Precipitation of Molybdenum as Molybdenum Sulfide

The precipitation of molybdenum as the sulfide can take place in two ways: either the acid solution may be precipitated by hydrogen sulfide gas, or the solution of ammonium thiomolybdate may be acidified with dilute acid.

(a) Precipitation of Molybdenum Sulfide from Acid Solutions

Place the molybdenum solution, slightly acid with sulfuric acid,[1] in a small pressure flask and saturate in the cold with hydrogen sulfide. Close the flask, heat on the water bath until the precipitate has completely settled, and filter after it has become cold. Wash the precipitate with very dilute sulfuric acid and finally with alcohol until the acid has been completely removed. Place the moist filter in a large porcelain crucible and dry upon the water bath. Cover the crucible and heat very carefully over a small flame until no more hydrocarbons are expelled. Then remove the cover, burn off the carbon from the sides of the crucible at as low a temperature as possible, and, by raising the temperature gradually, change the sulfide to oxide. The operation is finished when no more sulfur dioxide is formed. After cooling, add a little mercuric oxide suspended in water to the contents of the crucible, stir the mixture well, evaporate to dryness on the water bath, remove the mercuric oxide by gentle ignition, and weigh the residue of molybdenum trioxide. The mercuric oxide helps to remove particles of unburned carbon.

It is much easier to transform the molybdenum trisulfide into the oxide as follows: Filter off the sulfide into a Gooch crucible, wash with water containing sulfuric acid, and then with alcohol, and dry at 100° C. Place the crucible within a larger nickel one, cover with a watch glass,[2] and carefully heat over a small flame until the sulfide is for the most part changed to the oxide. As soon as the odor of sulfur dioxide can no longer be detected, remove the watch glass and heat the open crucible to a constant weight. The molybdenum oxide thus obtained always contains traces of SO_3, and consequently has a bluish appearance. The results, nevertheless, are excellent.

(b) Precipitation of Molybdenum Sulfide from Alkaline Solution

To the molybdenum solution add an excess of ammonium hydroxide and saturate the solution with hydrogen sulfide until it assumes a bright red color. Make acid with sulfuric acid and treat the precipitate as described under (a).

Separation of Molybdenum from the Alkaline Earths

Fuse the substance with sodium carbonate, extract the melt with water, and filter. The solution contains all the molybdenum as alkali

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[1] In some cases, e.g., for the separation of Mo from Ba, Sr, and Ca, it is necessary to effect the separation in a *hydrochloric* acid solution.

[2] To avoid loss by decrepitation.

molybdate, while the alkaline earths remain undissolved as carbonates. From the aqueous solution determine the molybdenum by one of the above methods.

Separation of Molybdenum from the Metals of the Ammonium Sulfide Group

Precipitate the molybdenum as sulfide (preferably from a sulfuric acid solution) by treatment with hydrogen sulfide under pressure (see p. 114). If the solution contains titanium, it is better first to add ammonia and ammonium sulfide, so that the metals of Group III will be precipitated and the molybdenum will remain in solution in the form of its thio salt. After filtration, precipitate the molybdenum as sulfide by the addition of acid (see p. 114, b).

Separation of Molybdenum from the Metals of Group II

(a) From Lead, Copper, Cadmium, and Bismuth

Make the solution alkaline with sodium hydroxide, add sodium sulfide, digest for some time in a closed flask, and filter. The molybdenum remains in solution as its thio salt, while the other metals are precipitated as sulfides. After filtering, acidify the solution with sulfuric acid and heat in a pressure flask until the precipitate has settled and the supernatant liquid appears colorless. After allowing to cool, filter off the molybdenum sulfide and convert to oxide, as described on p. 114.

(b) From Arsenic

Add ammonium hydroxide to the solution, which must contain the arsenic as arsenic acid, and precipitate the arsenic by magnesia mixture (see p. 83), and filter. Make the filtrate acid with sulfuric acid and precipitate the molybdenum as sulfide as described on p. 114.

Separation of Molybdenum from Phosphoric Acid

Precipitate the phosphoric acid from the ammoniacal solution as magnesium ammonium phosphate (cf. p. 83) and the molybdenum as sulfide in the filtrate (cf. p. 114, a). Another way is to saturate the ammoniacal solution with hydrogen sulfide, acidify with hydrochloric acid, and thus precipitate the molybdenum as sulfide. In this filtrate precipitate the phosphoric acid as magnesium ammonium phosphate under the customary conditions.

Determination of Molybdenum as Lead Molybdate[1]

Weigh out 0.5–5.0 g of the finely powdered ore into a 250-ml Erlenmeyer flask (not more than 0.15 g of Mo or 0.25 g of MoS_3 should be taken), and heat with 15 ml of concentrated nitric acid until the brown fumes are gone. Then add 10 ml of concentrated hydrochloric acid and evaporate to a small volume. Add 15 ml of 18 N sulfuric acid and evaporate to fumes of sulfuric acid. Cool, add 50 ml of water, and boil gently for a few minutes. Filter into a 150-ml beaker. Wash the $PbSO_4$ and SiO_2 residue with hot water, then 6 to 8 times with 4 N ammonia, and finally with hot water.

If arsenic is present add a little ferric sulfate at this point to make sure that 10 times as much iron as arsenic is present. Usually 0.3–0.4 g of the ferric salt is sufficient. This insures the precipitation of all the arsenic as ferric arsenate upon neutralization. Nearly neutralize the solution with ammonia, heat to boiling, and pour slowly into 75 ml of hot 9 N ammonia solution containing 3 g of sodium carbonate. The carbonate serves to precipitate alkaline earths if present. Stir well, and filter when the precipitate has settled. Wash with hot water. If arsenic is absent, omit the details described in this paragraph.

To the filtrate add 3 g of tartaric acid and saturate the alkaline solution with hydrogen sulfide. The tartaric acid is necessary to prevent the subsequent precipitation of vanadium and tungsten with the molybdenum. Filter off any precipitate that may form in this alkaline solution and wash with water containing hydrogen sulfide. To the filtrate add 6 N sulfuric acid until there is no further effervescence. Heat for a short time, filter off the MoS_3 precipitate, and wash with very dilute sulfuric acid saturated with hydrogen sulfide.

Dissolve this last sulfide precipitate in a little aqua regia and evaporate with hydrochloric acid to remove the nitric acid and the greater part of the excess acid. Dilute to 300 ml and neutralize with ammonia until alkaline to methyl orange. Then add 4–5 ml of 6 N hydrochloric acid, 10 g of ammonium acetate, and 2 ml of acetic acid. Heat to boiling and add 2 per cent lead acetate solution slowly from a buret, while stirring, until a drop of the solution tested on a spot plate will show no color change with fresh, 0.5 per cent tannin solution (Chapter XVII, Procedure 19). A brown color is obtained before all the molybdenum has been precipitated. Next add 2–5 ml excess lead acetate and 5–10 ml of acetic acid. Heat on the hot plate nearly to boiling for 15–20 minutes, filter while hot, and wash with hot dilute ammonium nitrate solution. Ignite carefully and weigh as $PbMoO_4$.

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[1] See *U. S. Bur. Mines, Bull.* 212, and *Descriptive Circ.* 6079.

Determination of Molybdenum in Steel

Solution of the Sample. *(a) Tungsten Absent.* Treat 2–5 g of sample (approximately 0.03 g Mo) with 100 ml of 6 N H₂SO₄ and heat until action ceases. Add 20 ml of 25 per cent (NH₄)₂S₂O₈ solution and boil 10 minutes to oxidize the molybdenum to the sexivalent state. Cool somewhat, add 5 g of tartaric acid, neutralize with ammonia, make acid with sulfuric acid, and add 10 ml of 18 N H₂SO₄ in excess for each 100 ml of solution.

(b) Tungsten Present. Treat enough sample to contain about 0.03 g Mo with 100 ml of 6 N HCl. Heat gently, and when most of the sample has dissolved add 25 ml of 6 N HNO₃ and boil gently until the tungstic acid residue becomes bright yellow. Dilute to 150 ml, heat to boiling, filter, and wash the residue with 1.2 N HCl. Save this residue and, after uniting it with any further deposit of WO₃, examine it for Mo as described in the next paragraph. To the solution add 15 ml of concentrated H₂SO₄, evaporate to fumes, cool, carefully dilute with 100 ml of water, and, if there is any residue of tungstic acid, filter it off, wash it with 0.36 N H₂SO₄, and combine it with the first residue.

Dissolve the combined tungstic acid residues in hot 5 per cent NaOH solution; wash the filter paper with hot water and finally with a little dilute H₂SO₄. Treat this solution separately with H₂S as described below for the main solution.

Precipitation with H₂S. To the solution add 5 g of tartaric acid, neutralize with NH₄OH, then add 18 N H₂SO₄ to an acid reaction and 10 ml in excess for each 100 ml of solution. Heat to boiling, and introduce a rapid stream of H₂S for about 20 minutes. Dilute with an equal volume of hot water and continue passing the H₂S for 5 minutes more. Digest at 60° for an hour. Filter and wash the MoS₃ precipitate with 0.36 N H₂SO₄ which is saturated with H₂S.

Precipitation with Lead Acetate. With a stream of water from a wash bottle, transfer the precipitate back to the original beaker, place this under the funnel, and dissolve any precipitate adhering to the filter by pouring through the filter four 5-ml portions of hot 6 N HCl containing a little Br₂. Finally wash the paper with hot water and reserve it for the next filtration. To the contents of the beaker add 20 ml of concentrated HCl and 3 g of NaClO₃. Boil gently until all the MoS₃ has dissolved, filter through the same paper that was used before, and wash with hot water. Reserve the filtrate.

Heat the filter and its contents in a porcelain crucible until all the carbon is consumed, cool, and digest the ash with a little, freshly prepared 5 per cent NaOH solution. Add the solution to the reserved filtrate.

Nearly neutralize the entire solution with NaOH and pour the slightly acid solution into 100 ml of boiling-hot 5 per cent, freshly prepared NaOH solution. Filter, wash the precipitate with hot water, and save the filtrate which contains practically all the Mo. To recover any Mo in the precipitate, dissolve it in hot 6 N HCl, nearly neutralize, and pour the solution into about 25 ml of hot 5 per cent NaOH solution. Filter and add this filtrate to the main solution.

Neutralize the solution with HCl and add 8 ml of 6 N acid in excess. Evaporate, if necessary, to 250 ml, and to the clear solution add 50 ml of a 20 per cent solution of ammonium acetate. Heat to boiling and, while stirring, add a 1 per cent solution of lead acetate which contains 10 ml of acetic acid per liter. If an appreciable quantity of Mo is present it is usually shown by the solution suddenly clearing when a slight excess of reagent has been added. Usually 10 ml of the reagent is sufficient. Boil 2–3 minutes, allow the precipitate to settle, and test with a little more of the reagent to make sure that all the Mo is precipitated as PhMoO$_4$.

If the precipitation is complete, boil for 10 minutes, let the precipitate settle, filter through an ashless paper, and wash with hot 2.5 per cent NH$_4$NO$_3$ solution until free from chloride.

If the precipitate is large, dissolve it in hot 6 N HCl, heat to boiling, nearly neutralize with ammonia until a slight permanent precipitate is obtained, add 10 ml of 50 per cent ammonium acetate solution, a little more lead acetate reagent, boil 2 minutes, allow to settle, filter, and wash as before.

Transfer the paper and precipitate to a weighed porcelain crucible, burn off the carbon carefully, and heat to dull redness. Cool and weigh as PbMoO$_4$.

SEPARATION OF ARSENIC, ANTIMONY, AND TIN FROM ONE ANOTHER

Arsenic from Antimony

For separating arsenic from other elements one of the following properties can be utilized: (1) Arsenic pentasulfide is less soluble than most other sulfides and can be formed by introducing hydrogen sulfide into a cold solution containing quinquevalent arsenic which has been made strongly acid by adding considerable concentrated hydrochloric acid. (2) Arsenic trichloride is easily volatilized from solutions containing trivalent arsenic and hydrochloric acid. (3) Arsenic in the quinquevalent state forms characteristic precipitates of MgNH$_4$AsO$_4$·6H$_2$O and Ag$_3$AsO$_4$.

The volatility of AsCl$_3$ is the basis upon which the best methods of separating arsenic from other elements rest. This volatility must also be borne in mind in all work with arsenic compounds, and solutions of quinquevalent arsenic should not be boiled long with hydrochloric acid as there is danger that some arsenic trichloride will be formed. Germanium is the only other element likely to be volatilized with the AsCl$_3$ under the conditions recommended for the analysis, and in those rare cases where germanium is present, it can be volatilized as GeCl$_4$ in a stream of chlorine; later the arsenic can be reduced and distilled off in a stream of hydrogen chloride gas.

(a) Volatilization Method of E. Fischer[1]

Principle. This separation depends upon the ready volatility of arsenic trichloride in a current of hot hydrochloric acid gas, under which conditions antimony chloride is not volatile if the temperature is kept below 105°. If the arsenic is present as arsenic acid, as is usual, the distillation must take place in the presence of some reducing agent.[2]

Procedure. Use an apparatus similar to that shown in Fig. 30 for this determination. In the course of analysis, the arsenic and antimony, as a rule, are obtained first as sulfides, and these should be dissolved in caustic potash solution and oxidized by chlorine. Instead of using
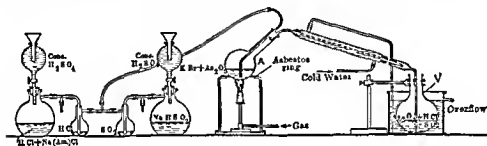
Fig. 30.

chlorine, the alkaline solution may be boiled with hydrogen peroxide or potassium percarbonate. If this method is followed for the oxidation, the boiling must be continued until there is no further evolution of oxygen.

Transfer the oxidized solution, by means of a long-stemmed funnel, to the 500-ml distilling flask, A, in which has been placed 1.5 g of potassium bromide.[3] Dilute the solution in the flask with 12 N hydrochloric acid to a volume of about 200 ml. The receiver, V, consists of a large flask of 1.5- to 2-liter capacity; keep it cold by circulating a stream of cold water. At the start place 800 ml of cold water in the beaker, and during the analysis keep cold water running through the condenser

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[1] Z. anal. Chem., 21, 266. The process as described in the modification of M. Rohmer, Ber., 34, 33 and 1565 (1901).

[2] Fischer used a ferrous salt, O. Piloty and A. Stock used hydrogen sulfide (Ber., 30, 1619), and Friedheim and Michaelis used methyl alcohol (Ber., 28, 1414).

[3] Instead of the potassium bromide, hydrogen bromide may be used which has previously been prepared by treating 1 g of bromine with sulfurous acid. It is not permissible to introduce the bromine into the flask, A, and convert it there to hydrogen bromide by introducing sulfur dioxide gas into the flask, because it is then possible for bromine vapors to get into the receiver by means of the air which is first expelled from the apparatus, and the bromine would oxidize the volatilized AsCl₃ and thus interfere with the subsequent determination of the arsenic by precipitation as the trisulfide, or by titration.

and have it overflow into the beaker containing the receiving flask. With the apparatus all connected as shown in the drawing, heat the distilling flask and distil in a current of hydrogen chloride,[1] meanwhile constantly passing a little sulfur dioxide into the flask. At the end of about 45 minutes, when the volume of liquid in A is reduced to about 40 ml, remove the flame and disconnect the T-tube between the two evolution flasks in order to prevent liquid from backing up into the wash bottles. Rinse off the adapter tube which connects the condenser with the receiver, and remove the receiver.

Place another receiver at the end of the apparatus and make a second distillation to make sure that all the arsenic has been volatilized.[2]
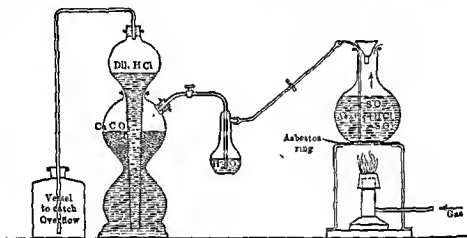
Fig. 31.

Then, for the determination of the arsenic, dilute the contents of the two receivers with hot water to a volume of about 1250 ml, and remove the excess of sulfurous acid by heating to boiling and passing a stream of carbon dioxide through the liquid as is shown in Fig. 31. When all the sulfur dioxide has been expelled (as can be shown by inserting a stopper with delivery tube into the flask so that the escaping vapors can be led into a dilute sulfuric acid solution of decinormal permanganate which will be decolorized by sulfur dioxide), allow the solution to cool and determine the arsenic as trisulfide according to the directions on p. 82, or titrate the arsenic with iodine.

To accomplish the titration, add 3 drops of phenolphthalein indicator solution to the solution and add solid potassium hydroxide until a per-

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[1] If there is any tendency to suck back, a little more sulfur dioxide should be introduced.

[2] Rohmer found that as much as 0.15 g arsenic was volatilized completely by one distillation.

manent pink color is imparted to the liquid. Then decolorize the solution by a few drops of hydrochloric acid, add 5 g of sodium bicarbonate, and titrate with decinormal iodine solution as described in Part II.[1]

Determine the antimony by treating the contents of the distilling flask with 2 or 3 g of tartaric acid, washing the solution into an Erlenmeyer flask, expelling the sulfur dioxide as above,[2] and determining the antimony gravimetrically by precipitating as the trisulfide according to the directions on p. 89, or volumetrically by titration with iodine as described in Chapter XV.

Remark. If the quantity of arsenic is not large, there is no need of distilling with a stream of HCl. A much simpler apparatus can be used and the procedure described on p. 125 followed.

(b) Precipitation of As_2S_5

The precipitation of As_2S_5 from strong hydrochloric acid solutions was described on p. 82.

Procedure. Starting with a precipitate consisting of the trisulfides of arsenic and antimony, dissolve this in caustic potash solution and oxidize exactly as described under the previous method. To the solution add acid, wash the acid solution into an Erlenmeyer flask, and cool by surrounding the flask with ice. In another flask likewise cool some 12 N hydrochloric acid. When both solutions are at 0°, dilute the arsenic-antimony solution with twice its volume of concentrated hydrochloric acid. Into this cold solution pass a rapid stream of hydrogen sulfide for 90 minutes. Stopper the flask and allow to stand an hour or more before filtering off the As_2S_5 through a Gooch crucible. Wash the precipitate with 4 N hydrochloric acid until 1 ml of the filtrate after being considerably diluted with water and tested with hydrogen sulfide shows no precipitation. Then wash with water and finally with hot alcohol. After drying at 110° C, weigh the precipitate as As_2S_5.

Dilute the filtrate from the arsenic sulfide with about 4 times as much water and saturate with hydrogen sulfide. Filter off the Sb_2S_5 into a Gooch crucible, dry at 280° C in a current of carbon dioxide, and weigh as Sb_2S_3 (p. 89).

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[1] A blank determination should be made with all the reagents that are used, and the iodine solution must be standardized in a solution as dilute as that in which the analysis is made.

[2] The escaping gas will not decolorize a solution of 2–3 ml dilute sulfuric acid and 1 drop of 0.01 N $KMnO_4$, when all the SO_2 is expelled.

(c) *Precipitation of $MgNH_4AsO_4 \cdot 6H_2O$*

Principle. The separation is based upon the fact that, if magnesia mixture is added to a solution of an alkali arsenate and antimonate containing tartaric acid only arsenic will be precipitated.

Procedure. Oxidize the solution obtained by dissolving the sulfides in aqueous caustic potash as described under (a). Make acid with hydrochloric acid and add 3 g of tartaric acid. Add an excess of ammonia; if a precipitate forms, it shows that an insufficient amount of tartaric acid is present. In this event decant off the clear solution, dissolve the precipitate by warming with tartaric acid, and mix the two solutions. To the clear, ammoniacal solution, add magnesia mixture (cf. p. 83, footnote) slowly with constant stirring. After standing 12 hours, filter off the precipitate of magnesium ammonium arsenate (it usually contains a little basic magnesium tartrate), and wash a few times with 1.5 N ammonia. Dissolve the precipitate in hydrochloric acid, heat to boiling, and reprecipitate by the addition of an excess of ammonia. After allowing to stand for 12 hours more, filter off the precipitate, wash with 1.5 N ammonia, and weigh as magnesium pyroarsenate as described on p. 83 or as $MgNH_4AsO_4 \cdot 6H_2O$ (cf. p. 84).

Remark. Arsenic can also be separated from tin according to the above method, except that more tartaric acid is necessary to prevent the precipitation of the tin than when antimony alone is present (cf. p. 124).

(d) *Precipitation as Ag_3AsO_4*[1]

Transfer the sulfides of antimony and arsenic to a platinum dish and dissolve in a little fuming nitric acid. Evaporate off most of the excess acid; add 2 ml of 45 per cent hydrofluoric acid and a little water. Heat until a clear solution is obtained, and dilute to 100 ml. Cover with a quartz glass, heat just to boiling, and treat with 5 g of $K_2S_2O_8$ added cautiously in small portions. Cool, add a little methyl orange indicator solution, and make neutral with ammonia. Heat to boiling and add a slight excess of silver nitrate solution. Cool, filter off the chocolate-brown Ag_3AsO_4 precipitate, and wash it with water containing 5 g of NH_4NO_3 and 0.25 g $AgNO_3$ per liter. Finally wash with a little alcohol. Test the filtrate with more silver nitrate and make sure that it is neutral to litmus. Determine the silver content of the precipitate either gravimetrically as chloride or volumetrically by the Volhard method. In either case dissolve the precipitate in a little dilute nitric acid.

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[1] L. W. McKay, *J. Am. Chem. Soc.*, **50**, 368 (1928).

Separation of Antimony from Tin

F. W. Clarke's Method,[1] Modified

Of all the known methods for the separation of antimony from tin, this is probably the most accurate. It depends upon the fact that antimony is completely precipitated from a solution containing oxalic acid, while stannic tin is not. Stannous sulfide, however, is decomposed by oxalic acid, forming an insoluble crystalline stannous oxalate, so that the tin must be in the stannic form.

Procedure. Usually it is a question of separating antimony from tin after these metals have been separated from the members of the copper group by means of alkali polysulfide; i.e., the tin and the antimony are in the form of the soluble thio salts.

To the solution of the thio salts in a 500-ml beaker containing not more than 0.3 g of the two metals, add an aqueous solution of 6 g of the purest caustic potash (one-third the sum of the weights of tartaric and oxalic acids to be added) and 3 g of tartaric acid (10 times the maximum weight of the two metals). To this mixture slowly add Perhydrol until the yellow solution is completely decolorized; then add 1 ml in excess and boil the solution for a few minutes to change any thiosulfate to sulfate and to decompose the greater part of the excess peroxide. As soon as the evolution of oxygen ceases, cool the solution somewhat, cover the beaker with a watch glass, and cautiously add a hot solution of 15 g pure recrystallized oxalic acid (5 g for 0.1 g of the mixed metals). This causes the evolution of considerable gas ($CO_2 + O_2$). Now, in order to remove all the excess hydrogen peroxide, boil the solution vigorously for 10 minutes. The volume of the liquid should amount to 80–100 ml. After this, introduce a rapid stream of hydrogen sulfide into the boiling solution; for some time there will be no precipitation, but only a white turbidity. After 5 or 10 minutes the solution becomes orange-colored and the antimony begins to precipitate; from this point take the time. At the end of 15 minutes dilute the solution with hot water to a volume of 250 ml; at the end of another 15 minutes remove the flame; and 10 minutes later stop the current of hydrogen sulfide. Filter off the precipitated antimony pentasulfide through a Gooch crucible which, before weighing and after drying, has been heated in a stream of carbon dioxide at 300° for at least 1 hour. Wash the precipitate twice by decantation with 1 per cent oxalic acid and twice with very dilute acetic acid before bringing it in the crucible. Both these wash liquids should be boiling hot and satu-

[1] Chem. News, 21, 124. Cf also Rössing, Z. anal. Chem., 41, 1; P. Henz, Z. anorg. Chem., 37, 18 (1903), Vortmann and Metzl, Z. anal. Chem., 44, 525 (1905).

rated with hydrogen sulfide. Weigh the Sb_2S_3 after the treatment described on p. 89.

To determine the tin, evaporate the filtrate to a volume of about 150 ml, nearly neutralize the excess of oxalic acid with potassium hydroxide, and deposit the tin electrolytically as described on p. 97.

According to Vortmann and Metzl,[1] antimony can be separated from tin by passing hydrogen sulfide into a solution containing hydrochloric and phosphoric acids of the proper concentration.

Separation of Arsenic from Tin and Antimony

(a) *Method of Fred. Neher*[2]

Dissolve the moist sulfides in freshly prepared ammonium sulfide, evaporate nearly to dryness in an Erlenmeyer flask, and oxidize with hydrochloric acid and potassium chlorate. From this solution precipitate the arsenic as sulfide under the conditions described on p. 82. In the filtrate from the arsenic pentasulfide all tho tin is found and can be precipitated as sulfide after diluting largely with water and passing in hydrogen sulfide. Ignite and change to the oxide as described on p. 97.

(b) *Method of W. Hampe*[3]

Dissolve the precipitated sulfides, as soon as possible after filtering and washing, in freshly prepared ammonium sulfide, evaporate the solution nearly to dryness, and oxidize with hydrochloric acid and potassium chlorate in a flask connected with a return-flow condenser.[4] Add tartaric acid and ammonia, and precipitate the arsenic with magnesia mixture as magnesium ammonium arsenate, according to p. 83. After allowing to stand 12 hours, filter off the precipitate, wash with 1.5 N ammonia, and, in order to remove a little magnesia, dissolve the precipitate in hydrochloric acid and reprecipitate by the addition of ammonia. After another 12 hours, filter off the precipitate and again wash with 1.5 N ammonia.

This precipitate can be converted into magnesium pyroarsenate and weighed in this form as described on p. 83. The transformation is somewhat tiresome, however, so that Hampe prefers to dissolve the precipitate in hydrochloric acid once more, to precipitate the arsenic by means of hydrogen sulfide, and then to determine the magnesium in

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[1] *Z. anal. Chem.*, 44, 533 (1905).
[2] *Z. anal. Chem.*, 32, 45 (1893).
[3] *Chem. Ztg.*, 18, p. 1900 (1894).
[4] So that no arsenic trichloride will be lost by volatilization.

the evaporated filtrate as magnesium pyrophosphate according to p. 256 or p. 257.

(c) Method of Plato-Hartmann[1]

In this interesting method the chlorides of arsenic, antimony, and tin, in the lower states of oxidation, are heated with a mixture of phosphoric and hydrochloric acids. Arsenous and antimonous chlorides distil by raising the temperature to 165°, but stannous chloride forms a complex with phosphoric acid and remains behind. According to Plato, tartaric acid is added to the first distillate and by a second distillation the arsenous chloride is removed. Hartmann prefers to precipitate the arsenic as trisulfide from a solution quite strongly acid and antimony as trisulfide in the partially neutralized filtrate. After the trichlorides of arsenic and antimony have been distilled from the solution containing hydrochloric and phosphoric acids, the tin is volatilized as stannic chloride by the addition of hydrobromic acid. The latter reacts with the hot, concentrated sulfuric acid and is to some extent oxidized into bromine which in turn oxidizes the tin to volatile stannic chloride.

For the distillations, the apparatus shown in Fig. 32 is suitable. On the extreme right of the drawing is shown a Kipp generator for producing carbon dioxide, connected through the wash bottle and the long glass tube to B into which acid can be made to drop from the funnel T. The lower part of B leads almost to the bottom of the flask A. The stopper of the flask is also fitted with a thermometer and a gas exit tube D, leading to the condenser P, which in turn is connected with the receiver E, in which the subsequent precipitation can also take place. The uncondensed vapors pass through the tube K, containing glass beads wetted with water, into the tubing R, which is connected with the tower G containing pieces of marble. In this way the acid vapors are neutralized so as not to be obnoxious.

It is advisable to wind cord around D to keep the vapors from being cooled too much by the air; for the same reason the neck of the flask A should be covered with asbestos paper.
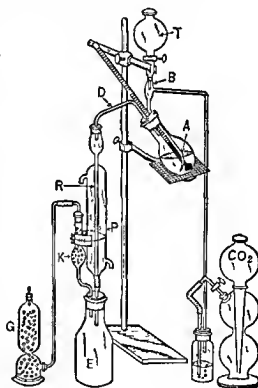

FIG. 32.

Procedure. If the sample is an alloy, weigh out 1 g of the fine borings into the flask A, Fig. 32, add 6 ml of concentrated sulfuric acid, and heat until decomposition is complete. Of arsenic, antimony, and tin sulfides, place the precipitate and filter in the flask and add enough sulfuric acid

[1] Plato, Z. anorg. Chem., 68, 26 (1911); Z. anal. Chem., 50, 641 (1911); Hartmann, Z. anal. Chem., 58, 148 (1919).

so that the mass is not quite dry after the carbonization of the filter; continue heating until the sulfuric acid solution is colorless, or a light straw color, and volatilize any sulfur in the neck of the flask by heating carefully with a flame. Evaporate off the excess sulfuric acid, leaving about 6 ml in the flask. If the carbon of the filter is not oxidized sufficiently there will be too much foaming during the subsequent distillation.

Cool, add 7 ml of aqueous phosphoric acid, d 1.70, again cool, add 10 ml of concentrated hydrochloric acid, and connect the apparatus with a little water in the receiver. Introduce a slow stream of carbon dioxide, begin heating the flask, and cause concentrated hydrochloric acid to drop into the flask so that the volume of liquid in the flask does not change much during the distillation. Keep the temperature at 155–165°. The arsenic trichloride distils readily, but it may take 2 or 3 hours to distil all the antimony trichloride. To test for antimony, disconnect the receiver and collect about 20 drops of fresh distillate. To this add a little hydrogen sulfide water and ammonia water to neutralize some of the acid; if no orange precipitate forms, antimony is absent.

When all the antimony has been volatilized as chloride, stop distilling and disconnect the receiver. Taking a fresh receiver, continue the distillation using a mixture of one-fourth pure hydrobromic acid, d 1.40, and three-fourths concentrated hydrochloric acid in the dropping funnel. If bismuth is present, keep the temperature below 145°. Distil until no test for tin is obtained with 1 ml of distillate. A little sulfur dioxide is always present in the distillate, being formed by the interaction of hydrobromic and sulfuric acids. There is, therefore, always some sulfur precipitated when the H_2S water is added, but this milky turbidity can be distinguished from a precipitate of yellow stannic sulfide that forms more quickly. The distillation should not be stopped until there is no sign of yellow precipitate in the test.

To determine arsenic in the first distillate, introduce hydrogen sulfide and treat the precipitate of arsenic trisulfide as described on p. 82.

To determine antimony in the filtrate which contains hydrogen sulfide, neutralize with ammonium hydroxide until a permanent precipitate of orange antimony sulfide forms. Add a little more ammonium hydroxide, but not enough to make the solution ammoniacal, dilute with an equal volume of hot water, and saturate with hydrogen sulfide gas. Treat the antimony trisulfide precipitate as directed on p. 89.

To determine tin, take the second distillate, dilute with a little water, and add ammonium hydroxide until the stannic hydroxide precipitate does not redissolve well on stirring. Saturate with hydrogen sulfide, allow to stand over night, and treat the precipitate as directed on p. 94. Filter-paper pulp aids in filtering the stannic sulfide.

Separation of Antimony from Arsenic and Tin

(a) Method of Rose

Heat the sulfides of arsenic, antimony, and tin with fuming nitric acid in a large covered beaker until the sulfur is completely oxidized, and remove the excess of acid by evaporation on the water bath. Treat the slightly moist residue with concentrated sodium hydroxide solution, and transfer the contents of the dish to a silver crucible. Add a little solid sodium hydroxide, and dry the contents of the crucible in an air bath. Place the silver crucible in a larger porcelain one, heat over a Méker burner, and keep the contents of the smaller crucible liquid for about 20 minutes. Cool, extract the melt with water, add one-third as much alcohol to precipitate sodium metantimonate completely, and after allowing to stand for 12 hours filter off the precipitate, wash with 50 per cent alcohol, dissolve in HCl, and determine antimony as sulfide (p. 89). Acidify the filtrate containing all the arsenic and tin with hydrochloric acid, so that stannic arsenate is precipitated. Without filtering, conduct hydrogen sulfide into the liquid, filter off the precipitated sulfides of tin and arsenic, oxidize with hydrochloric acid and potassium chlorate, and separate the arsenic from the tin as described on p. 124.

(b) Method of Hampe

Oxidize the moist sulfides with hydrochloric acid and potassium chlorate, and determine the arsenic as described on p. 83.

In the combined filtrates from the magnesium ammonium arsenate precipitate the antimony and tin by hydrogen sulfide, after making the solution acid. Separate these according to one of the methods already described; cf. p. 123.

(c) GOLD AND THE PLATINUM METALS

PLATINUM, PALLADIUM, OSMIUM, RUTHENIUM, RHODIUM, AND IRIDIUM

GOLD, Au. At. Wt. 197.2

Gold is always determined as the metal itself. There are three cases to distinguish:

1. The gold is present in solution.
2. The gold is alloyed with copper and silver.
3. The gold is present in an ore.

1. Gold Is Present in Solution

Usually gold is deposited as metallic gold from its solutions and weighed after filtering and washing.

For the deposition of gold numerous reducing agents can be used, such as ferrous sulfate, oxalic acid, sulfurous acid, formaldehyde, and hydrogen peroxide. If the gold is to be precipitated by means of either *ferrous sulfate* or *oxalic acid*, no free nitric acid can be present in the solution. If some is present, it must be removed by repeated evaporation with concentrated hydrochloric acid and the solution then diluted with water. To this dilute solution add a large excess of clear ferrous sulfate solution, cover the beaker, and heat its contents for several hours on the water bath. Then filter off the precipitate, wash first with water containing hydrochloric acid until the iron is completely removed, and then with pure water. Dry the precipitate, transfer as completely as possible to a porcelain crucible, add the ash of the filter, ignite, and weigh the gold. In this way gold can be separated from most metals, even platinum, but not from silver. If silver is present, as of course it never is in a dilute hydrochloric acid solution, remove it by the addition of hydrochloric acid, filter off the precipitated silver chloride, and treat the filtrate as above described.

To precipitate gold by means of *oxalic acid*, adjust the acidity so that the solution contains the equivalent of 2 ml of concentrated HCl and 5 drops of concentrated H_2SO_4 in each 100 ml, add the oxalic acid, and boil 10 to 15 minutes. In the filtration of precipitated gold, the filter paper must fit tightly to the funnel along the upper edge and sometimes, the addition of some ashless filter-paper pulp is advisable.

If a gold solution is treated with caustic alkali solution and then with formaldehyde, or, better still, hydrogen peroxide,[1] the gold is soon precipitated quantitatively, even in the cold. By boiling, the finely divided gold collects together and assumes a reddish brown color. The reaction takes place according to the following equation:

$$2AuCl_3 + 3H_2O_2 + 6KOH = 6KCl + 6H_2O + 3O_2 + 2Au$$
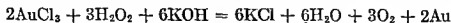
If the gold is deposited by this method from very dilute solutions it is obtained in such a finely divided condition that it passes through the filter. If, however, the solution is boiled until the excess of hydrogen peroxide is completely destroyed and it is then acidified with hydrochloric acid, the gold can be readily filtered. Gold can be separated from platinum by this method.

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[1] Vanino and Seeman, *Ber.*, **32**, 1968 (1899).

2. The Gold Is Alloyed with Silver and Some Copper

Gold present in alloys is most rapidly and most accurately determined in the dry way. The principle of the method is very simple. Too much copper should not be present as high-copper alloys cannot be cupelled.

If a gold-silver alloy is melted in the air with lead upon a " cupel " (a very porous vessel made of bone-ash or magnesia) the lead and copper are oxidized, the oxides fuse and are absorbed by the cupel, while all the gold and silver are left behind in the form of a metallic button, which is weighed. The silver is afterwards separated from the gold by the action of nitric acid, which dissolves the silver but leaves the gold behind. If the weight of the gold that is left undissolved is deducted from the weight of the gold-silver button the weight of the silver is obtained.

To obtain accurate results a number of precautions must be taken. By the cupellation of the alloy some noble metal is always lost, the amount increasing in proportion to the amount of lead used and the temperature. Furthermore, small amounts of the noble metal are absorbed by the cupel, and this loss is greater the smaller the quantity of lead used. This second loss amounts to much less than the former one occasioned by the use of too much lead. *Consequently, in every gold cupellation an unnecessary excess of lead must be avoided.*

Experience has shown that the richer a gold-silver alloy is in base metal the more lead is necessary for the cupellation. Furthermore, in the separation or *parting* of gold from silver by means of nitric acid, it is necessary to remember that the separation is quantitative only if the alloy consists of 3 or more parts of silver to 1 part of gold. If less than 3 parts of silver are originally present for 1 part of gold, it is necessary to add pure silver until this proportion is reached. This operation is known as *quartation* or *inquartation*. If a gold-silver alloy, in the form of foil, consisting of 3 parts of silver to 1 of gold, is treated with nitric acid, the gold remains behind as a brownish scale; if more silver is present, it is left as a fine powder, unless the acid is extremely dilute. Sometimes a little silver may remain with the gold after the treatment with acids and this causes high results in weighing the residual gold; often error due to incomplete removal of silver more than balances the loss of gold during the cupellation.

From what has been said, it is clear that accurate results can be obtained only when the correct amount of lead is present in the alloy that is cupelled, and when the gold and silver are present in the proper proportion; i.e., it is necessary to know the approximate composition of the

In the case of a greenish yellow alloy, inquartate[1] with 2 parts of silver; and for a distinctly yellow or reddish yellow alloy, inquartate with $2\frac{1}{2}$ parts of silver.

Treatment of the Gold-Silver Button

Remove the gold-silver button from the cupel with the " button tongs," clean with a stiff brush (" button brush "), and hammer upon an anvil to a round disk about 1 mm thick (Fig. 35, *a*). Heat this upon a fresh cupel and quickly cool by placing it upon a piece of brass foil and rolling it between two steel rollers to a long strip (Fig. 35, *b*); again heat and roll[2] up as shown in Fig. 35, *c*. Place this little roll in
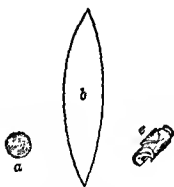
Fig. 35.   Fig. 36.

a small flask (Fig. 36, I), cover with 30–40 ml of nitric acid (*d* 1.188) free from chloride, heat to boiling, and keep boiling gently for 10 minutes. Pour off the acid, replace by the same quantity of stronger acid (*d* 1.295), and repeat the above treatment. After this pour off acid and wash the button, decanting three times with distilled water. Fill the flask with water, cover with an annealing cup (or, lacking this, an ordinary porcelain crucible may be used), and quickly invert (Fig. 36, II); the gold will pass into the cup. Remove the flask by first raising its mouth to the level of the water in the crucible and then slide it off at right angles and skilfully turn the flask right side up. Pour off the water from the gold and place the crucible in the back part of the

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[1] Cf. p. 129.

[2] By hammering, the gold-silver alloy becomes so brittle that it cannot be converted to a smooth-margined roll, and on the subsequent treatment with nitric acid, little pieces would probably drop off. Heating the metal again and then quickly cooling it restores its original softness.

muffle for a short time; the gold dries and is changed from its former brown and soft condition into a harder, beautiful yellow substance. Cool and weigh. By subtracting the weight of the gold from the weight of the gold and silver together, the amount of silver is determined.

Determination of Gold in Ores

Principle. The very finely ground and sifted ore is mixed in a No. 9 French crucible with lead oxide, charcoal, and some suitable slag-forming material. The charcoal reduces a part of the lead oxide to metal which alloys with the noble metal and sinks to the bottom in the form of a button, while the foreign substances pass into the slag After cooling, break the crucible, hammer off the slag, cupel the lead button, and part the silver-gold button in the usual way. The noble metal should be extracted with as little lead as possible, for with an unnecessarily large amount of lead some gold is lost during the cupellation.

The amount of lead reduced from the litharge depends largely upon the nature of the ore. Sulfide ores act strongly reducing, as is shown by the following equations:

$$PbS + 2PbO = SO_2 + 3Pb$$
$$FeS_2 + 5PbO = 2SO_2 + FeO + 5Pb$$
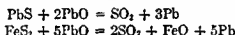
In such cases less charcoal (or in some cases none at all) should be added than would be otherwise necessary to produce the right amount of lead. Sometimes, when considerable sulfide is present, it is necessary to neutralize its action by the addition of oxidizing agents.

Reducing ores are recognized by their color: they are gray, bluish black, or yellow (pyrite, etc.). Reddish brown ores (Fe_2O_3) usually act oxidizing:

$$Fe_2O_3 + C = CO + 2FeO$$

in which case more charcoal must be added to the charge.

The best results are obtained if the lead button weighs about 18 g when obtained from 30 g of ore [1] In order that such a button may be obtained, it is usually necessary to make a preliminary assay of the ore. But above all, it is necessary that the purity of the reagents used should be tested.

Testing the Reagents

The ordinary reagents necessary for a gold assay are:

Litharge (PbO)

Litharge, the most important reagent, is a basic flux, for it forms a readily fusible silicate with the silicic acid of the ore. At the same time, it is a desulfurizing agent, as is shown by the above reaction.

The litharge used must be dry and free from minium, Pb_3O_4, which oxidizes silver, carrying it into the slag, so that low results would be

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[1] This amount is usually sufficient; with very rich gold ores 10–15 g is enough, whereas with very poor ores as much as 120 g may be used to advantage.

obtained in the silver determination. The litharge should be free from silver (which it almost never is), or its silver content must be known; this is determined once for all by the following experiment: Mix 120 g of litharge, 60 g of sodium bicarbonate, and 2 g of argols (crude $KHC_4H_4O_6$) upon a sheet of glazed paper; place the mixture in a No. 9 French crucible and cover with a layer of finely powdered, dry common salt. Place the covered crucible in a hot coke-oven.

As soon as the contents of the crucible have reached the state of quiet fusion, remove the crucible from the fire, gently tap its walls with the tongs, and tap lightly upon its bottom to knock down any small particles of lead adhering to the sides and to make all the free metal collect together on the bottom in the form of a button.

After cooling break the crucible, remove the slag from the lead button by hammering it upon an anvil, and subject it to cupellation, using a cupel weighing only a few grams more than the button itself. Weigh the resulting silver button, and deduct this weight of silver whenever the corresponding amount of litharge is used in an assay.

Sodium Bicarbonate ($NaHCO_3$)

Anhydrous Borax ($Na_2B_4O_7$)

These require no testing.

Charcoal

The reducing power is determined as follows: Mix 60 g of litharge, 15 g of sodium bicarbonate, and 1 g of charcoal, as in the testing of litharge, in a French crucible No. 9, cover with common salt, and fuse. After cooling, determine the weight of the lead button; this expresses in terms of lead the reducing power of the charcoal.

One gram of charcoal should reduce about 30 g lead.

Niter (KNO_3)

serves as an oxidizing agent. Its oxidizing power expressed in terms of lead is determined as follows: Mix 3 g of niter (potassium nitrate), 60 g of litharge, 1 g of charcoal, and 15 g of sodium bicarbonate; fuse as before, and determine the weight of the lead button. If it was found that 1 g of charcoal would reduce P g of lead, and if p g of lead were obtained in this experiment, then the difference $P - p$ shows the amount of lead that was oxidized by 3 g of niter, or the oxidizing power of the niter.

One gram niter oxidizes about 4 g lead.

Common Salt

Heat table salt in a large Hessian crucible until it melts, and pour the contents of the crucible into a shallow iron mold with a raised edge. Powder and preserve in a stoppered flask.

After the reagents have all been tested the next step is the

Preliminary Assay

Weigh out 5 g of the finely powdered and sifted ore and mix with 80 g of litharge, 20 g of sodium bicarbonate, and 5 g of borax. Place the mixture in a crucible and cover with a layer of common salt. After fusing, cooling, and hammering off the slag, as already described, weigh the lead button.

Since in an ordinary assay about 30 g of ore is taken, the weight of the lead button now obtained multiplied by 6 will give the weight of the button from the real assay. Four cases will be considered.

(1) The Lead Button Weighs 3 g

A button obtained from 30 g of ore would weigh 18 g. In this case, assay the ore with the following proportions of flux: 80 g of litharge, 20 g of sodium bicarbonate, and 5 g of borax.

(2) The Lead Button Weighs Less than 3 g

Evidently the ore has a slight reducing action, but not enough to yield a button weighing 18 g when 30 g of ore is used; it is, therefore, necessary to add charcoal to the flux.

Example. Assume that the lead button obtained by the preliminary assay weighed 1 g, then the button obtained from 30 g of ore would weigh 6 g. In order to obtain a button weighing 18 g it is necessary to add enough charcoal to supply 12 g of lead. If 1 g of charcoal is found to reduce 30 g of lead, then it is necessary to add 12 ÷ 30 g = 0.4 g of charcoal.

(3) The Lead Button Weighs More than 3 g

In this case the ore has a strong reducing power, and to obtain the lead button of the right weight it is necessary to add some niter.

Example. Suppose the button to weigh 6 g; this would mean a 36-g button when 30 g of ore is used; i.e., 18 g too much lead would be produced. We must add, therefore, enough niter to oxidize this 18 g of lead. If the oxidizing power of 1 g of niter is found to be 4 g of lead, then 18 ÷ 4 = 4.5 g of niter must be added to the flux.

Remark. Ores which have a very strong reducing power would frequently require the addition of enough niter to cause the contents of the crucible to boil

over. In such a case, place 40–50 g in a " roasting dish," roast in a muffle, and from this roasted ore take portions for the preliminary and final assays. The results, however, must be expressed in terms of the unroasted ore.

(4) No Lead Button Is Formed

The ore is either neutral or possesses an oxidizing action. Repeat the assay using 1 g of charcoal, and base the final assay from the results now obtained.

Final Assay

For convenience, it is customary to weigh out the ore in *assay-ton* units. Ore is usually weighed in avoirdupois tons and gold in troy ounces. The assay report usually gives the ounces troy contained in a ton avoirdupois. Since there are 29,166 troy ounces in an avoirdupois ton, the assay ton is made equal to 29.166 g. Then if 1 assay ton of ore is used each milligram of gold obtained will represent *1 ounce per ton.* For weighing out the ore an inexpensive balance (pulp balance) can be used. It should be capable of taking a load of 200 g but need not be sensitive to less than 1 mg. For weighing the gold or silver buttons, a *button balance* sensitive to 0.01 mg should be used.

For the final assay use from 0.1 to 5 assay tons of ore (according to the amount of gold present) and the corresponding amount of the various fluxes. Otherwise the procedure is exactly the same as in the preliminary assay. Cupel the lead button and part the weighed silver-gold button as described on p. 132.

PLATINUM, Pt.   At. Wt. 195.2

Platinum is best determined as metallic platinum. The following three cases will be considered:

1. The platinum is present in a hydrochloric acid solution either alone or together with other metals, but other platinum metals are absent.
2. The platinum is present alloyed with gold and silver.
3. The platinum is alloyed with small amounts of the platinum metals together with small amounts of base metals.

1. The Platinum Is Present in Hydrochloric Acid Solution Either Alone or Together with Other Metals

The platinum is either precipitated from the solution as ammonium chloroplatinate, $(NH_4)_2PtCl_6$, which is decomposed by ignition and the residual platinum weighed; or the platinum is precipitated as metal by the addition of reducing agents to the solution; or finally the platinum is precipitated as sulfide by conducting hydrogen sulfide into the

not solution and changed to platinum by ignition. The first two methods serve to separate platinum from most other metals; the third serves to separate platinum only from the metals of the alkali, alkaline earth, and ammonium sulfide groups, and not from members of the hydrogen sulfide group.

(a) Precipitation of Platinum as Ammonium Chloroplatinate

Reduce the volume of the solution as much as possible by evaporation; nearly neutralize with ammonia; add an excess of ammonium chloride and considerable alcohol. Allow the mixture to stand 12 hours under a glass bell jar. Filter through an asbestos filter tube 10–15 cm long and wash with 80 per cent alcohol until a few drops of the filtrate leave no residue on being evaporated to dryness on a platinum foil. Dry the precipitate by conducting a stream of air, warmed to about 90°, through the tube. After cooling weigh the tube, introduce a plug of ignited asbestos[1] and again weigh; thus the weight of the asbestos plug is found. Conduct a stream of dry hydrogen through the tube, and heat the tube carefully until no more hydrochloric acid is evolved and all the ammonium chloride has been driven off; then cool the tube in a desiccator and weigh.

Instead of filtering the precipitate upon asbestos, an unweighed ashless paper filter may be used. Place the moist precipitate and the filter in a large porcelain crucible so that the apex of the filter paper points upward, and heat very carefully, as otherwise there can be a considerable loss by spattering. At first dry the precipitate by gently heating the partly covered and inclined crucible with a tiny flame under the cover until the odor of alcohol has disappeared. Take care not to burn the alcohol. When all the alcohol has evaporated, slowly raise the temperature until the crucible is at a strong red heat. During the whole operation there must be no visible escape of vapors from the crucible. The decomposition is complete when there is no longer a penetrating odor arising from the crucible. Now place the crucible in an upright position and ignite with free access of air until the carbon from the filter paper is completely burned. Often a slight deposit of platinum[2] will

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[1] Ammonium chloroplatinate decrepitates during the heating. To prevent loss of substance heat it between two asbestos plugs.

[2] By means of the dry distillation of the filter, carbon monoxide is formed; and by the decomposition of the ammonium chloroplatinate, chlorine is set free. These two gases act upon the metallic platinum and form volatile compounds ($PtCl_2 \cdot CO$, $PtCl_2 \cdot 2CO$, and $2PtCl_2 \cdot 3CO$), which, however, are later decomposed by the aqueous vapor. This causes the deposit of platinum in the upper part of the crucible. In order to avoid loss, a large crucible should be used.

he found in the upper part of the crucible and upon the cover, so that
the cover must always be weighed with the crucible.

Remark. If it seems likely that the precipitate of ammonium chloroplatinate
is contaminated with other substances (e.g., sodium chloride, etc.) the precipitate
can be dissolved in hot water after it has been washed with alcohol and dried. The
platinum may then be determined, by boiling with a little mercury, filtering,
washing with dilute hydrochloric acid and then with water, igniting the residual
Pt, and finally weighing.

The results obtained by this method are satisfactory but somewhat
lower than the true values; the following process is more accurate:

(b) Precipitation of Platinum by Reducing Agents

Free the solution from any excess of acid by evaporation and transfer
to an Erlenmeyer flask the neck of which is ground to fit a return-flow
condenser. Neutralize the solution with ammonia, add an excess of
formic acid and a little ammonium acetate, dilute to 200 ml, and heat
to about 80° on the water bath until the evolution of carbon dioxide
has nearly ceased. Now connect the flask with the return-flow con-
denser, and boil for 24 hours. Filter off the precipitated metal, wash
first with dilute hydrochloric acid then with water, dry, ignite, and
weigh.

2. Determination of Platinum in Alloys

Platinum is now used a great deal in jewelry, and there are so many
useful alloys of platinum that the analysis has become of importance.
The platinum content is almost always determined by dry assay.

Weigh out 0.1 g of the alloy and make a trial assay to determine
the approximate platinum content. Cupel twice with 1-g portions of
lead at a high temperature (well back in the hot muffle), weigh the
resulting button, and part with sulfuric acid as described below. For
the analysis proper, weigh out 0.25 g of alloy; add 1.25 g of pure silver
and the same quantity of copper. Cupel at a white heat, using 15 g
of lead if the alloy is nearly pure platinum and reducing the quantity
of lead by 0.15 g for each per cent of alloyed metal but using at least 2 g.

After the cupellation place the button on a fresh cupel and heat 2–5
minutes in the hottest part of the muffle. Hammer out the button
and roll it until it is 0.2 mm thick. Part the button in a small Jena
flask, using 20–30 ml of concentrated sulfuric acid which has been
diluted with 22 per cent of water by volume. Heat the metal with the
sulfuric acid for 15 minutes at 240°. Nitric acid could not be used
for the parting as it dissolves some platinum as well as silver. By

boiling platinum with pure concentrated sulfuric acid, 7.7 mg is dissolved in an hour but dilution prevents the dissolving. By keeping the temperature at 240° there is no appreciable loss of platinum.

After the heating allow the acid to cool, carefully decant off the liquid, and repeat the acid treatment twice more. To avoid loss by bumping during the second and third treatments, wind a piece of pumice with platinum wire and drop it into the flask. After the third treatment, decant off the acid and wash the residual platinum twice by decantation with water. During the decantation some platinum always flows off with the liquid. Save the washings, therefore, filter through a small filter, ignite, and weigh in a crucible. Transfer most of the platinum to a porcelain crucible, rinse off the pumice, and evaporate off the water. Ignite and weigh.

Separation of Platinum from Gold

Parting with sulfuric acid leaves gold, if present, with the platinum. Parting with nitric acid does not dissolve platinum in the absence of silver but, if 3 parts by weight of silver are present for each part of gold and platinum, the platinum gradually dissolves.

Procedure. Cupel the platinum-gold button, obtained by the above method of assaying, with 3 times its weight of pure silver and 1 g of lead. Hammer and roll the resulting button and part with 6 N nitric acid. Weigh the button, inquartate with 3 parts of silver, and again cupel with 1 g of lead. This time part with 9.5 N nitric acid. Repeat the inquartation and parting until a constant weight of gold is obtained.

Instead of separating gold and platinum in this way, the button can be dissolved in aqua regia and the gold precipitated by ferrous sulfate as described on p. 128 or the gold may be thrown down from an alkaline solution by means of hydrogen peroxide. It may be necessary to dissolve the gold in aqua regia and repeat the precipitation. To determine the platinum, precipitate it as sulfide by introducing hydrogen sulfide into the hot acid filtrate and weigh as metal after ignition in a porcelain crucible.

PALLADIUM, Pd.   At. Wt. 106.7

In the older methods of analysis, palladium was usually determined as metal. Although some palladic salt is formed when the metal is dissolved in aqua regia, it is reduced to bivalent palladous chloride, $PdCl_2$, on evaporating with concentrated hydrochloric acid. From a slightly acid solution of palladous chloride, the free metal can be deposited easily by heating with sodium formate solution or by passing carbon monoxide into the cold, slightly acid solution. The deposited metal can be filtered off, ignited, and weighed. Palladium also forms some insoluble salts that

can be used for quantitative analysis. Thus palladous cyanide, $Pd(CN)_2$, palladous iodide, PdI_2, and palladous α-nitroso-β-naphthol, $Pd(C_{10}H_6NO_2)_2$, have been recommended for determining palladium. In the first two cases, the similarity of palladous salts to silver salts will be noticed, and in qualitative analysis palladium is precipitated in the first group. In the case of the α-nitroso-β-naphthol compound, the analogy to cobalt will be noticed. This is not surprising, for palladium, like cobalt, belongs in the eighth group of the periodic table of the elements. Today, the most characteristic reagent for palladium is dimethylglyoxime, which is used so much for determining nickel, another eighth-group element. By means of this reagent, it is possible to separate palladium from the other platinum metals; and the precipitate can be weighed. Gold must be absent or it will precipitate as metal. The only objection that can be raised to dimethylglyoxime as a reagent for palladium is the fact that the precipitate is very voluminous and when much of it is present it may be difficult to handle. In such cases precipitation of the cyanide or of the iodide can be used. Both $Pd(CN)_2$ and PdI_2 are sufficiently insoluble to provide satisfactory separations. The iodide is soluble in an excess of potassium iodide solution so that care must be taken to use only a slight excess of reagent, and rhodium iodide, RhI_3, may precipitate if much rhodium is present. Potassium iodide also gives a deep red color with H_2PtCl_6 on account of the formation of H_2PtI_6; this reaction has been recommended for detecting platinum.

1. Determination with Dimethylglyoxime

Procedure. To the moderately acid solution (it can be $0.25 N$ in HCl or HNO_3) containing not more than 0.1 g of Pd in 250 ml, add at room temperature a 1 per cent solution of dimethylglyoxime in 95 per cent alcohol. For each milligram of palladium present, use about 0.25 ml of the reagent (0.0025 g of solid). Allow the solution to stand for half an hour at about 40° or for an hour at room temperature and then filter through a weighed Gooch crucible. To the filtrate add a little more of the reagent to make sure that the precipitation is complete. Wash the orange-yellow precipitate of $Pd(C_4H_7N_2O_2)_2$ thoroughly, first with cold and then with hot water, dry at 110°, and weigh. The precipitate contains 31.67 per cent of palladium.

If it is desired to repeat the precipitation, as is sometimes necessary when much platinum is present, filter through a paper filter and digest the precipitate with 25 ml of aqua regia which has been diluted with an equal volume of water. Dilute, filter, burn the filter, digest the ash with aqua regia, dilute, and filter into the main solution.

If more than 0.1 g of palladium is present, it is well to work with an aliquot part of the solution, or an ashless filter paper can be used for filtering off the bulky precipitate. Transfer to a weighed porcelain crucible, dry, ignite slowly, and cool in a stream of hydrogen. Finally uncover the crucible and heat momentarily to redness to drive off most of the occluded hydrogen, cool, and weigh as Pd. If ignited in air, the precipitate is weighed as palladous oxide. Or dissolve the precipitate in formic acid, warm the

contents on a hot plate to evaporate off the excess formic acid, and finally weigh as Pd.

2. Precipitation of Palladium by Formic Acid

To the fairly dilute solution add sodium formate solution, cover with a watch glass, and heat carefully over a free flame. Carbon dioxide is evolved, and shortly the palladium is precipitated as a fine black powder: $PdCl_2 + HCO_2Na = NaCl + HCl + CO_2 + Pd$. The finely divided metal is appreciably soluble in hydrochloric acid. After the evolution of gas has ceased, therefore, add sodium carbonate solution until a neutral or faintly alkaline reaction is obtained. Filter and wash the palladium with hot water. Place the moist filter and precipitate in a porcelain crucible and carefully ignite, finally using the full heat of the burner. Cool and weigh. As a rule, there is a slight superficial oxidation of the metal as shown by blue or violet colorations, but the increase in weight is so small that it can be neglected.

3. Precipitation of Palladium as Palladous Cyanide

Nearly neutralize the solution with sodium carbonate and add an excess of mercuric cyanide: $PdCl_2 + Hg(CN)_2 = HgCl_2 + Pd(CN)_2$. Heat on the water bath until there is no more odor of hydrocyanic acid; allow the light yellow precipitate to settle; wash it by decantation and on the filter with cold water. Dry, ignite, and weigh as Pd.

Separation of Palladium from Platinum

Evaporate the hydrochloric acid solution to dryness. If any nitric acid was present, add more hydrochloric acid and again evaporate to dryness, because it is necessary for the success of this separation that all the palladium shall be in the bivalent condition. Otherwise, insoluble $(NH_4)_2PdCl_6$ will be formed together with the corresponding platinum compound.

To the residue add a slight excess of solid ammonium chloride. Moisten with a little water, and after a short time add some saturated ammonium chloride solution (38 per cent). Stir well, allow to stand for some hours, then filter off the $(NH_4)_2PtCl_6$ precipitate. Wash with strong ammonium chloride solution and treat the precipitate as described on p. 137.

In the filtrate determine the palladium as the palladous salt of dimethylglyoxime.

Separation and Determination of the Six Platinum Metals

Platinum is the best-known member of a group of six noble metals. Their chemical properties are quite similar, and the problem of separating them completely from one another is not an easy one. Arranged in the order of their atomic weights they

hy stopping the flow of hydrogen for a moment, then start the flow again and allow the crucible to cool to room temperature in an atmosphere of hydrogen. Now replace the H_2 with an inert gas such as CO_2, as otherwise there will be some oxidation when the reduced metal is first exposed to the air. Weigh as Os.

II. Separation and Determination of Ruthenium

Transfer the solution remaining in the flask A, Fig. 37, to a beaker or casserole and evaporate to dryness on the steam bath. Add 5–10 ml of concentrated HCl and again evaporate; repeat the addition of HCl and evaporation until no more oxides of nitrogen are evolved. Dissolve the last residue in 25 ml of water, add 10 ml of concentrated H_2SO_4, and evaporate on the hot plate until H_2SO_4 vapors are evolved. Cool, carefully dilute with 10 ml of water, and transfer the solution back to the distilling flask A; if any platinum has deposited during the evaporation make sure that this is washed into the flask. Dilute with water to 100 ml, add 150 ml of 10 per cent $KBrO_3$ solution, and distil as described under (I) with fresh portions of $HCl~SO_2$ in the three receivers. To make sure that excess SO_2 is present in the receivers, add from time to time a little saturated SO_2 solution through the funnel T_2. Remember to flush out the tubing under T_1 occasionally. After 90 minutes' slow distillation in a gentle current of air, add 25 ml more of 10 per cent $KBrO_3$ solution and distil for another hour. This will serve to remove 0.15 g of ruthenium.

Combine the three portions of absorbing solution in the flasks B, C, and D and evaporate in a beaker on the steam bath. To the moist residue add 10 ml of concentrated HCl and digest in the covered beaker on the steam bath for an hour. Add 50 ml of water and heat to boiling to dissolve the difficultly soluble ruthenium salt which forms during the evaporation. Filter off any small silicious residue (from the glass), wash the filter with 0.1 N HCl, dilute the solution to 200 ml, and precipitate the ruthenium as hydrated RuO_2 as described for osmium (see I, 2) but in place of the bromophenol blue indicator add 3–4 drops of 0.04 per cent bromocresol purple indicator solution, which changes from yellow to purple at about $pH = 6$. When this point is reached boil about 5 minutes to coagulate the precipitate.

Convert the RuO_2 to Ru as in the case of osmium (I, 2) but with these differences: Use ashless filter paper for filtering, and remove the last traces of precipitate from the walls of the beaker with filter paper. Wash the precipitate with hot 1 per cent $(NH_4)_2SO_4$ in place of NH_4Cl and finish with a 2.5 per cent solution. Ignite the precipitate carefully in air in a weighed porcelain crucible and then in hydrogen. After the first ignition in hydrogen, cool and leach the residue with water to remove traces of soluble salt and again ignite in air and in hydrogen. Weigh as Ru.[1]

III. Separation and Determination of Platinum

1. **Preparation of the Solution.** (a) The solution in the distilling flask from which OsO_4 and RuO_4 have been removed will contain platinum, palladium, and iridium together with H_2SO_4, $NaHSO_4$, Br_2, and possibly some undecomposed

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[1] Rogers, Beamish, and Russell, *Ind. Eng. Chem., Anal. Ed.*, 12, 561 (1940), prefer to absorb the RuO_4 in 3 per cent H_2O_2 (free from acetanilide). Then, upon making the solution 0.2 N in HCl and HBr and boiling, the Ru can be precipitated with a slight excess of thioglycolic-β-aminonaphthalide dissolved in a little alcohol (a little more than 2 moles of the thionalide per mole of Ru). After washing with alcohol the precipitate can be ignited in air and then in hydrogen and weighed as Ru.

bromate. Transfer to a beaker and carefully add concentrated HCl to decompose any bromate. Evaporate the solution on the steam bath and add more HCl to make sure that all bromate is decomposed. If the distilling flask is stained with IrO_2, clean it with 5–10 ml of aqua regia and, before adding this acid to the main solution, evaporate with HCl to decompose nitroso compounds. Finally evaporate the entire solution as far as possible on the steam bath and then dilute to 300 ml with water.

(b) *If a solution containing no osmium or ruthenium is to be analyzed*, leave out everything up to this point and start the analysis as follows: Evaporate to a moist residue on the steam bath and, if nitric acid or a nitrate was present, add to the residue 5 ml of concentrated HCl and evaporate again. Add 2 g of NaCl and 5 ml of concentrated HCl and evaporate to dryness. To this residue add 2 ml of concentrated HCl and dilute with water to 300 ml.

2. Removal of Palladium, Rhodium, and Iridium as Hydrated Dioxides. Heat the solution to boiling and add 20 ml of 10 per cent $NaBrO_3$ solution. Carefully add 10 per cent $NaHCO_3$, until the solution, which is usually a dark green in color, shows evidence of the formation of a permanent precipitate. Test the acidity of the hot solution from time to time by allowing a drop of 0.01 per cent bromocresol purple to run down a stirring rod which has just been lifted out of the solution. Enough $NaHCO_3$ has been added when the pH of the solution has been raised to 6; then the indicator solution will change from yellow to blue when it meets the drop of solution that adheres to the bottom of the stirring rod. Now add 10 ml more of 10 per cent bromate solution and boil 5 minutes. To make sure that all palladium is precipitated, increase the pH of the solution to about 8 by adding more $NaHCO_3$ solution dropwise until a faint pink color is produced in a test drop with a drop of 0.01 per cent cresol red indicator solution. Add a final 10-ml portion of 10 per cent bromate solution and boil 15 minutes. Filter through a porcelain or glass filtering crucible which has a solid side and porous bottom.

Rinse the beaker and wash the precipitate with 1 per cent NaCl solution of pH between 6 and 7; the acidity should not exceed the point at which bromocresol indicator changes from blue to yellow. Use the filtrate for the determination of platinum and the precipitate for palladium, rhodium, and iridium.

The precipitate of hydrated PdO_2, RhO_2, and IrO_2 may contain a little platinum. To recover this, place the crucible, precipitate, and stirring rod in the beaker used for the precipitation. Cover with a watch glass and add 10–20 ml of 12 N HCl. Heat on the steam bath until all the dioxides have dissolved. Carefully *lift up the crucible* with the stirring rod, wash it with water, and transfer to a small beaker. Add to it 5 ml of 12 N HCl and heat on the steam bath to leach out small quantities of metal chlorides in the porous bottom of the crucible. Pour off the acid into the main solution and leach once more with acid. To the combined solution add 2 g of NaCl, evaporate to dryness on the steam bath, dilute to 300 ml with water, and repeat the precipitation of the hydrated oxides of Pd, Rh, and Ir. Two such precipitations serve to effect complete separation of platinum from palladium, rhodium, and iridium.

3. Precipitation of Platinum as PtS_2. Add 20 ml of 12 N HCl to each of the filtrates from the hydrolytic precipitation described under (2). Heat until there is no more evolution of CO_2, combine the two solutions, and evaporate to dryness. Make certain that all hromate is destroyed by adding 5 ml more HCl and again evaporating. Dissolve the residue in 100 ml of water, filter if necessary, and wash with 0.1 N HCl. Add 20 ml of 12 N HCl, heat to gentle boiling, and pass a rapid stream of H_2S through the solution. Allow the solution to cool somewhat while continuing the passage of the gas. Filter through a paper filter, wash with 0.1 N HCl, and transfer the dried

PtS_2 precipitate to a weighed porcelain crucible. Ignite carefully, leach the residual metal with 0.1 N HCl, filter, ignite again, and weigh as Pt. The precipitate will contain a very little sulfide.

In work of the highest accuracy, dissolve the metal in aqua regia, remove nitroso compounds by adding HCl and evaporating to a moist residue, dilute, filter, wash the residue with 0.1 N HCl, dilute to 100 ml, and add 3 g of sodium acetate and 1 ml of formic acid for each 0.25 g of Pt. Boil gently until the deposited platinum is well coagulated and the supernatant liquid is colorless. Filter, wash with a hot 1 per cent NH_4Cl solution, and heat in a porcelain crucible. Leach with acid as above to remove any soluble salt, filter, and ignite again. Weigh as Pt.

IV. Separation and Determination of Palladium

Dissolve the precipitate of hydrated dioxides obtained in III, 2, with HCl as described for the purification of the first precipitation of dioxides, filter the solution, and dilute to 400 ml. The solution can be as much as 3.5 N in HCl or HNO_3. Add a sufficient volume of 1 per cent solution of dimethylglyoxime in 95 per cent ethyl alcohol to precipitate all the palladium (and provide a slight excess — for 0.1 g of Pd use 25 ml of reagent). Set aside for an hour, filter into a weighed Gooch crucible, wash with 0.1 N HCl and then with water, dry at 110°, and weigh as $PdC_8H_{14}N_4O_4$ with 31.67 per cent Pd. The precipitate is quite bulky, and if more than 0.15 g of Pd is present it is best to use an aliquot part of the solution. With small quantities of palladium an excess of 10 per cent reagent is recommended, but if a large quantity of palladium is present, a 10 per cent excess of solid dimethylglyoxime will contaminate the precipitate.

V. Separation and Determination of Rhodium

Dilute or concentrate the filtrate from the palladium precipitate to exactly 500 ml and use half for the rhodium determination. To this add 10 ml of concentrated H_2SO_4 and 3 ml of concentrated HNO_3. Evaporate until heavy fumes of H_2SO_4 are evolved, cool, add more HNO_3, and again heat to fumes. Continue this treatment until no more charring results and all the organic matter has been destroyed. Dilute the cooled solution with 20 ml of water and again evaporate to fumes to destroy any nitroso compounds that might interfere in the determination of rhodium.

Dilute the cooled solution to 200 ml and bring it to boiling. Add dropwise a solution of $TiCl_3$ (Chapter XVI, Procedure 3) until a drop of the supernatant liquid appears slightly purple. It is easy to find the end point if the beaker is held over a 100-watt lamp and the liquid is stirred. The metallic rhodium quickly coagulates into a spongy mass. If much iridium is present, the end point can be determined by the lack of formation of any more precipitate and by the appearance of an orange color in the solution. Boil 2 minutes, filter through paper, and wash the rhodium with 0.9 N H_2SO_4 at room temperature.

Place the filter and precipitate in a 300-ml Erlenmeyer flask, add 10 ml of concentrated H_2SO_4, char gently, and add 5 ml of concentrated HNO_3. Heat and destroy organic matter as described in the previous paragraph, and again precipitate the rhodium as before with $TiCl_3$. Redissolve the rhodium as before, and, after the removal of organic matter, dilute the sulfuric acid with 20 ml of water and add 10 ml of concentrated HCl. Boil the solution 15 minutes to get the rhodium into a state

from which it can be precipitated as sulfide. During the treatment the color of the solution will change from yellow to rose. Filter and wash with 0.1 N HCl.

Dilute the solution to about 450 ml, precipitate the rhodium as sulfide (Rh_2S_3 or $Rh(SH)_3$), and ignite to metal as described for platinum under III, 3.

VI. Determination of Iridium [7]

The iridium can be determined in the filtrate from the rhodium precipitation with $TiCl_3$. This involves (a) removal of the excess titanium with cupferron (see p. 155), (b) destroying the organic matter by treatment with $H_2SO_4 + HNO_3$ as described under V, (c) precipitating the iridium as hydrated IrO_2 as described under III, and (d) igniting the hydrated IrO_2 first in the air and finally in hydrogen as described for osmium under I, 2. This method is capable of high accuracy, but it is much simpler to take the filtrate from the palladium determination, make up to a definite volume, and use one aliquot part for the rhodium determination and another for determining rhodium and iridium together, as follows:

Precipitate the rhodium and iridium as hydrated dioxides as described under III, 2, but for washing the precipitate use a hot 1 per cent NH_4Cl solution which is neutral to bromothymol blue instead of the NaCl solution. Impregnate the dried filter and precipitate with a few drops of saturated NH_4Cl solution to prevent deflagration, and carefully ignite to a mixture of oxides. Heat this in hydrogen as described under I, and weigh the metallic residue of **Rh + Ir**. Make a correction for the quantity of Rh present as found under V.

When the above procedure was tested by numerous analyses made at the National Bureau of Standards for quantities up to about 0 2 g of each metal, the results were excellent. Two grams of platinum is easily handled.

CHAPTER III

GROUP III OF CATIONS

ALUMINUM, CHROMIUM, TITANIUM, IRON, URANIUM, NICKEL, COBALT, ZINC, AND MANGANESE

(a) DIVISION OF THE SESQUIOXIDES

ALUMINUM, CHROMIUM, IRON, TITANIUM, AND URANIUM

ALUMINUM, Al. At. Wt. 26.97

Forms: Al_2O_3, $AlPO_4$, $Al(C_9H_6ON)_3$

1. Determination as Al_2O_3

To determine aluminum as oxide, it is precipitated as the hydrated oxide which, as van Bemmelen has shown, is really $Al_2O_3 \cdot xH_2O$ rather than the hypothetical $Al(OH)_3$.

The hydrated oxide is amphoteric and tends to form colloidal solutions. Because of its amphoteric nature it is best precipitated, as Blum[1] has shown, by keeping the hydrogen-ion concentration at about 10^{-7}, as it is in pure water. Owing to the colloidal nature of the precipitate it is advisable to have ammonium salt in the solution and to wash the precipitate with water containing ammonium salt. The ammonium salt also prevents the precipitation of magnesium hydroxide by repressing the ionization of ammonium hydroxide.

Procedure. To the solution containing at least 5 g of ammonium chloride per 200 ml, or an equivalent quantity of hydrochloric acid, add a few drops of methyl red indicator (0.2 per cent alcoholic solution) and heat just to boiling. Add 6 N ammonium hydroxide until the color of the solution changes to a distinct yellow. Boil for 2 minutes and filter promptly. Wash the precipitate thoroughly with hot, 2 per cent ammonium nitrate solution. Ignite in an open crucible, cool, and weigh as Al_2O_3.

Since Al_2O_3 is hygroscopic and difficult to weigh unless it has been heated above 1100°, it is best to finish the ignition in an electric furnace which is heated to 1200°. The chief cause of high results, however, is not so much the absorption of moisture as it is contamination with silica from the action of the reagents on glass.

The ammonia should be freshly distilled When kept for any length of time in glass bottles it invariably contains a little dissolved silica which precipitates when

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[1] *J. Am. Chem. Soc.*, 38, 1282 (1916).

the ammonia is neutralized. Because of the solvent effect of acids and bases on glass, only glass of the borosilicate type should be used in the chemical laboratory.

According to Britton, aluminum hydroxide begins to precipitate at $pH = 4.14$ and the precipitate is dissolved at $pH = 10.8$. The above treatment with ammonium hydroxide serves to keep the pH within these limits; methyl red changes color at $pH = 4.4$-6.0. Most separations of aluminum from other metal ions are based upon the regulation of the pH. A salt of a weak acid added to the aqueous solution of an aluminum salt will serve to react with H^+ produced by hydrolysis and favor the completion of the reaction. The reaction is also helped if the weak acid is unstable and breaks down as fast as it is formed because, in accordance with the mass-action law, a reaction is favored by the removal of any product formed. Chancel[1] recommended sodium thiosulfate as a suitable salt:

$$2Al^{+++} + 6H_2O \rightarrow 2Al(OH)_3 + 6H^+$$

$$6H^+ + 3S_2O_3^{--} \rightarrow 3SO_2 \uparrow + 3S + 3H_2O$$
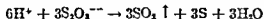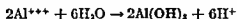
Chancel's Procedure. Add to the dilute, neutral solution (about 0.1 g Al in 200 ml) an excess of sodium thiosulfate and boil until all traces of SO_2 are expelled. Add 6 N ammonium hydroxide[2] until its odor is barely perceptible after blowing away the vapors, and continue boiling a little longer. Filter off the precipitate of $Al(OH)_3$ and S, wash it with hot 2 per cent ammonium nitrate solution, and ignite in a porcelain crucible. Such a precipitate of hydrated Al_2O_3 is much denser than that produced by direct precipitation with ammonia and it is very easy to filter and wash.

Alfred Stock[3] accomplished the same thing by adding a mixture of potassium iodate and iodide. The reaction

$$IO_3^- + 5I^- + 6H^+ = 3H_2O + 3I_2$$

is very sensitive to hydrogen ions, and, moreover, the free iodine can be removed easily by adding sodium thiosulfate

$$I_2 + 2S_2O_3^{--} = S_4O_6^{--} + 2I^-$$

Stock's Procedure. The solution in which the aluminum is to be determined should be very slightly acid; if more acid is present add sodium hydroxide solution until a slight permanent precipitate is obtained. Redissolve by means of a few drops of hydrochloric acid. Add equal volumes of a 25 per cent potassium iodide solution and a saturated potassium iodate solution (about 7 per cent KIO₃). After about 5 minutes, decolorize the solution by the addition of a 20 per cent sodium thiosulfate solution and add a little more of the potassium iodide and iodate mixture to make sure that enough is present. Add 1 or 2 ml

[1] *Compt. rend.*, 46, 987; *Z. anal Chem.*, 3, 391.
[2] If the addition of ammonia is omitted, the solution will retain traces of aluminum.
[3] *Ber.*, 1900, 548.

more of sodium thiosulfate solution and heat the mixture half an hour on the water bath. The pure white precipitate settles out well and can be filtered through a filter with relatively wide pores, washed with hot 2 per cent ammonium nitrate solution, ignited, and weighed as Al_2O_3.

Remark. The presence of calcium, magnesium, or boric acid does not interfere with the above determination, but if phosphoric acid is present, aluminum phosphate is precipitated. It is obvious that the method cannot be employed in the presence of organic substances such as tartaric acid, citric acid, or sugar, which prevent the precipitation of hydrated alumina.

Wynkoop[1] and Schirm[2] used ammonium nitrite as a suitable salt of a weak acid.

$$2Al^{+++} + 6H_2O \rightarrow 2Al(OH)_3 + 6H^+$$

$$6H^+ + 6NO_2^- \rightarrow 6HNO_2 \qquad 6HNO_2 \rightarrow 3H_2O + 3NO + 3NO_2$$
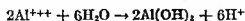
Wynkoop and Schirm's Procedure. If the solution is acid, add ammonia until the precipitate first formed dissolves only slowly on stirring. Add an excess of a 6 per cent solution of pure ammonium nitrite,[3] dilute the solution to 250 ml, and boil until no more fumes of nitrous oxides are evolved (about 20 minutes). Filter off the precipitate, wash with hot 2 per cent ammonium nitrate solution, ignite wet in a platinum crucible, and weigh as Al_2O_3.

Remark. In the presence of more than 1 per cent of ammonium salts, these are hydrolyzed enough so that the solution remains acid and the precipitation of the aluminum is incomplete even after long boiling. In such cases it is necessary to add some NH_4OH to accomplish complete precipitation.

2. Determination as AlPO₄

If a solution containing Al^{+++}, alkaline-earth ion, and phosphoric acid is carefully neutralized, $AlPO_4$ will form before $Al(OH)_3$ or alkaline-earth phosphate. If, however, the pH is raised a little higher, the precipitate is likely to become one of alkaline-earth phosphate and $Al(OH)_3$. In the ferric state, iron behaves like aluminum, and in the ferrous state like alkaline earth.

It is quite common practice to determine aluminum in the presence of iron by reducing the iron to the ferrous state by sulfurous acid or sodium thiosulfate, adding ammonium phosphate, and then continuing the treatment with sodium thiosulfate as in the method of Chancel described on p. 149. The results are not entirely satisfactory, but Lundell and Knowles[4] have shown that the determination of small quantities of aluminum as phosphate can give very accurate and reproducible results. Their procedure is as follows:

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[1] *J. Am. Chem. Soc.*, 19, 434 (1897).

[2] *Chem. Ztg.*, 1909, 877.

[3] Sometimes the reagent contains a little barium which should be precipitated with ammonium sulfate before using it in an analysis.

[4] *J. Am. Chem. Soc.*, 14, 1136 (1922).

To 400 ml of a solution containing sufficient acid to make it 0.3 N in HCl, add 1 g of $(NH_4)_2HPO_4$, or more if this does not provide a tenfold excess. Prepare some macerated filter pulp by tearing up ashless filter paper into small pieces and shaking the paper in a stoppered flask with a little water until a creamy emulsion is obtained. Add some of this paper pulp to the solution to aid in the filtration of the $AlPO_4$ precipitate. Add a few drops of methyl orange indicator solution and enough ammonium hydroxide to make the color of the stirred solution yellow. Then make acid with 1 ml of 6 N HCl, heat to boiling, and to the boiling solution add 30 ml of 25 per cent ammonium acetate solution. Boil 5 minutes, filter, and wash the precipitate with 5 per cent ammonium nitrate solution until it is practically free from chloride. Ignite in an open porcelain crucible and weigh as $AlPO_4$.

3. Determination with 8-Hydroxyquinoline

The use of this reagent is discussed briefly under "Magnesium," in Chapter V. The aluminum salt of *oxine* can be formed in dilute acetic acid solutions which are buffered with ammonium acetate. The precipitate is easier to filter than aluminum hydroxide or phosphate, and some useful separations of aluminum from other elements can be accomplished with this organic reagent.

Procedure. Heat the solution, containing not more than the equivalent of 0.1 g Al_2O_3 and one or two drops of mineral acid per 100 ml, to about 70° and add an excess of the reagent (cf. "Magnesium"). Slowly add 2 N ammonium acetate solution until a permanent precipitate is formed, and then add 20–25 ml more. Allow the precipitate to settle, filter through a weighed Gooch crucible, wash with cold water, dry at 120–140°, and weigh as $Al(C_9H_6ON)_3$ containing 11.1 per cent of Al_2O_3. The precipitate can also be dissolved and the 8-hydroxyquinoline determined volumetrically (cf. "Magnesium").

4. Determination of Small Quantities of Aluminum

The most satisfactory test for very small quantities of aluminum is the formation of a red lake with aurin tricarboxylic acid, to which dye the trivial name *aluminon* has been given. This test (see Vol. 1) can be made the basis of a colorimetric determination of aluminum by comparing the result obtained in the unknown solution with that obtained under similar conditions with known quantities of aluminum.

The test is best made by adding the reagent to an acetic acid solution containing aluminum and then adding an ammoniacal solution of ammonium carbonate. Under these conditions the final color of the dye alone is a pale yellow but the presence of aluminum causes a pink to deep red color.

A similar lake is formed with beryllium. Iron, the chief interfering element, must be absent because small quantities of iron give a purplish red tint. Large quantities of phosphate prevent the formation of the aluminum lake. Silicon, bismuth, lead,

antimony, mercury, and titanium give white precipitates. Large quantities of alkaline earths, basic salts, or hydroxides of chromium, yttrium, lanthanum, cerium, neodymium, erbium, zirconium, scandium, or thorium give red lakes but, fortunately, these are either dissolved or decolorized by ammonium carbonate. Cadmium, zinc, manganese, nickel, and cobalt give no precipitate. Reducing agents cause a fading color, but small quantities can be present if the color comparison with standards is made promptly. In short, the colorimetric determination of less than 0.1 mg of aluminum by means of *aluminon* is very satisfactory when no interfering ion is present but there are so many possibilities of interference that anomalous results are often obtained. The results are perfectly satisfactory in dilute solutions containing only aluminum salt in solution but in practice the chief problem lies in removing the interfering substances without, at the same time, removing a part of the aluminum.[1]

Colorimetric Procedure. For the test, prepare a solution containing 0.005 to 0.1 mg of aluminum in 20–30 ml of 0.5 N hydrochloric acid. Usually this represents an aliquot part of a more concentrated solution. Iron, beryllium, and large quantities of any of the above-mentioned interfering elements must be absent. Add 10 ml of 6 N acetic acid and 5 ml of a 0.2 per cent solution of *aluminon*. Slowly add, while stirring, a 10 per cent solution of $(NH_4)_2CO_3$ in 6 N NH_4OH until an excess of 5–10 ml is present (about 15 ml should be sufficient). Compare the color with standards which contain known quantities of aluminum with the same quantities of hydrochloric acid, acetic acid, *aluminon*, and ammonium carbonate reagent as were used in the test. Nessler tubes are convenient for the comparison, which is best made by looking downward through the entire solution against a white surface.

Aluminum is precipitated by tannin in the presence of alkali acetate as a voluminous tannin adsorption complex, and the precipitation is not prevented by tartaric acid. This procedure is described later (see p. 222).

IRON, Fe.   At. Wt. 55.85

Forms: Ferric Oxide, Fe_2O_3, and Metallic Iron

Determination as Fe_2O_3

1. By Precipitation with Ammonia

The precipitation of ferric iron by means of ammonium hydroxide can be accomplished as described under "Aluminum," but when only iron is present it is not necessary to keep the solution so near the neutral point because ferric hydroxide is not appreciably dissolved by an excess of ammonia and does not form a colloidal solution when washed with a moderate amount of hot water. The same precautions as described under "Aluminum" should be taken with regard to the use of freshly distilled ammonium hydroxide and the use of the best grades of glass that are not

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[1] Cf. Lundell and Knowles, *Ind. Eng. Chem.*, 18, 60 (1926); Yoe and Hill, *J. Am. Chem. Soc.*, 49, 2395 (1927).

attacked to any extent by dilute bases. The precipitate is rather bulky; an ordinary 9-cm filter will hold only about 0.2 g of iron as hydrated oxide.

Procedure. Heat the solution to about 70°, and at a volume of 200–300 ml precipitate hydrated ferric oxide by the addition of a slight excess of 6 N ammonium hydroxide. Allow the precipitate to settle and wash it twice by decantation with 50-ml portions of hot water. Transfer the precipitate to the filter with the aid of a rubber policeman and wash it on the filter with hot 2 per cent ammonium nitrate solution until free from chloride. Do not wash with ammonium chloride solution because ferric chloride is volatile upon ignition. Ignite slowly and carefully in an open porcelain or silica crucible and weigh as Fe_2O_3.

Remarks. It is not advisable to heat the precipitate over the blast because Fe_3O_4 is formed at high temperatures. This magnetic oxide is also formed if the carbon of the filter is not consumed at a low temperature When once formed it cannot be changed back to the less stable Fe_2O_3 by heating. The color of the ignited oxide does not indicate the presence of magnetite, for pure ferric oxide is nearly black after strong ignition. The ignited oxide is difficultly soluble in dilute hydrochloric acid but can be dissolved by long digestion with concentrated hydrochloric acid on the water bath.

The formation of magnetic iron oxide during the ignition of ferric hydroxide is said to be prevented by stirring some ashless filter-paper pulp (see p 151) into the liquid after the precipitation by ammonia.

The wash bottle shown in Fig 16 on p 35 is useful for work with hot water or with bad-smelling wash liquids It is well to wind the neck of the wash bottle with heavy curtain cord, if it is to be used for hot water.

If the iron is in solution either as the ferrous or the ferric salt of a volatile acid, it can be readily converted into ferric oxide by evaporation with sulfuric acid and ignition of the residue.

2. Determination as Metallic Iron

Iron may be determined by electrolysis, but this method offers no advantages over the gravimetric method just described or the volumetric process (see Part II).

In the analysis of oxidic iron ores or of mixtures of considerable iron oxide with comparatively little alumina, titanium dioxide, or silica, the following method is accurate and rapid.[1]

Weigh the finely powdered[2] substance in a porcelain boat. Introduce the boat into a tube of difficultly fusible glass and heat to redness in a stream of dry hydrogen until no more drops of water condense on the cool, front end of the tube, and the contents of the boat appear

[1] Rivot, Ann. chim. phys., [3] 30, 188 (1850); Ann., 78, 211 (1850).

[2] Ferric oxide after having been powdered and ignited is so hygroscopic that the porcelain boat should be placed within a weighing beaker with ground-glass top immediately after removing it from the desiccator, and then weighed.

gray and not black. By this means the ferric oxide is reduced to metallic iron:

$$Fe_2O_3 + 3H_2 = 3H_2O + 2Fe$$
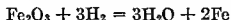
After cooling in the stream of hydrogen, again weigh the boat and its contents after they have remained some time in a desiccator. The loss in weight p represents the amount of oxygen originally combined with the iron, from which the amount of iron can be calculated:

$$\frac{2Fe}{3O} \cdot p = 2.327p = \text{weight of iron}$$

Remark. In attempting to reduce ferric oxide to iron by means of hydrogen, it is very important to heat the oxide to bright redness. At a dull red heat, the oxide is, to be sure, reduced to metal, but in such cases black pyrophoric iron is formed which cannot be exposed to the air and weighed without becoming oxidized. By heating to bright red heat, however, the iron becomes gray, is no longer pyrophoric, and can, if allowed to cool in the stream of hydrogen, which is subsequently replaced by carbon dioxide, be safely weighed in the air without fear of oxidation.

Although this method is extremely simple, and the corresponding oxides of aluminum, chromium, titanium, zircon, etc., are not reduced under the same conditions, it should be used with caution and only when the ferric oxide greatly predominates in a mixture of oxides. Otherwise the reduction of the iron is incomplete on account of some of the ferric oxide being enclosed within the particles of foreign oxide. This has been proved by the work of Daniel and Leherle[1] and by Treadwell and Wegelin. Moreover, the above computation shows that the error in determining the weight of reduced iron is multiplied by 2 33 in the computed weight of iron.

It is more accurate to dissolve the metallic iron in dilute sulfuric acid out of contact with the air and determine the amount present volumetrically by titrating with potassium permanganate solution.

3. By Precipitation with Cupferron

Cupferron, the ammonium salt of phenylnitrosohydroxylamine, has the formula $C_6H_5N \cdot NO \cdot ONH_4$. It found valuable use in quantitative analysis because it precipitates ferric iron, copper, zirconium, (hafnium), quadrivalent uranium, titanium, vanadium, quadrivalent tin, columbium, and tantalum. Precipitation takes place in the presence of considerable mineral acid, and the reagent is useful in separating the above-mentioned elements from aluminum, beryllium, phosphate, borate, manganese, nickel, and sexivalent uranium, all of which are likely to precipitate more or less completely when iron is thrown down as hydrated ferric oxide by the addition of ammonia. The use of cupferron was recommended strongly by O. Baudisch.[2]

[1] *Z. anorg. Chem*, 34, 393 (1903).

[2] *Chem. Ztg.*, 33, 1298 (1909). See also Baudisch and King, *Ind. Eng. Chem.*, 3, 629 (1911); Schroeder, *Z. anorg. Chem*, 72, 89 (1911); Nissenson, *Z. angew. Chem.*, 23, 969 (1910); R. Fresenius, *Z. anal. Chem.*, 50, 35 (1911); Lundell and Knowles, *Ind. Eng. Chem.*, 12, 344 (1920); Auger, *Compt. rend.*, 170, 995 (1920); Mariel and Kamm, *J. Am. Chem. Soc.*, 41, 276 (1919); Holladay and Cunningham, *Trans. Am. Electrochem. Soc.*, 43, 329 (1923); Kling and Lassieur, *Compt. rend*, 170, 1112 (1920); N. H. Furman, *Ind. Eng. Chem*, 15, 1071 (1923); Pinkus and Claessens, *Bull. soc. chim. Belg.*, 31, 413 (1927); H. Pied, *Compt. rend.*, 179, 897 (1924).

The reagent is used in the form of a 6 per cent aqueous solution. The solution should be made up as needed for it decomposes slowly with the formation of nitrobenzene. The dry reagent should be kept in a cool, dark place, preferably under a bag of ammonium carbonate suspended from the stopper of the bottle. Germuth[1] states that the stability of the aqueous solution is increased by the addition of 50 mg aceto-phenetidide ($C_6H_4 \cdot OC_2H_5 \cdot NH \, C_2H_5O$) per liter.

The precipitates formed can be regarded as salts of phenylnitrosohydroxylamine in which the NH_4 radical of the reagent is replaced by the cation which is precipitated. In accordance with Werner's valence theory, the metal " is co-ordinated both with the oxygen of the OH group (by principal valences) and with the oxygen of the NO group (by subsidiary valences)."[2] On this basis, the ferric salt is a non-ionizable

compound of the coordination formula $\left[\left(C_6H_5N \left\langle \begin{array}{c} NO \cdot \\ O \end{array} \right\rangle \right)_3 Fe \right]$.

The trivial name, cupferron, was suggested by Baudisch because it precipitates copper and iron from acid solutions and separates them from aluminum, chromium, manganese, etc. When the cupferron precipitates of iron and copper are washed with dilute ammonia, the iron compound is converted into insoluble hydrated ferric oxide and the copper compound dissolves with the formation of blue copper-ammonia ions. In the original filtrate, the excess cupferron can be destroyed by evaporating the solution and heating with sulfuric and nitric acids.

Procedure. To 200 ml of solution containing 0.2 g or less of iron in the ferric state, add 20 ml of 12 N HCl or 10 ml of concentrated sulfuric acid. Cool to about 10° and slowly introduce the cold 6 per cent cupferron solution while stirring until no more precipitation takes place. An excess of reagent is indicated by the formation of a temporary cloud of a fine, white precipitate which redissolves as contrasted with the flocculent and insoluble cupferron iron precipitate. When this white precipitate of phenylnitrosohydroxylamine forms, add about a quarter as much more of the reagent to make sure that a liberal excess is present. Stir in a little macerated ashless filter-paper pulp, allow the precipitate to settle for about 15 minutes, and then filter. Wash the precipitate first with cold 2 N HCl (or H_2SO_4) containing 1.5 g cupferron per liter. Then wash with dilute ammonia, to remove any copper and convert the iron to hydrated ferric oxide, and finally with water. Dry, ignite, and weigh as Fe_2O_3.

The cupferron precipitate can be washed with water until free from acid and ignited directly without the treatment with dilute ammonia. This requires more attention as the precipitate on being heated tends to liquefy and effervesce. If the cupferron precipitate sticks to the sides of the beaker it can be loosened by adding a little ether and the iron recovered by pouring the ether into dilute ammonia. The precipitation with cupferron will take place in the presence of tartaric acid, but it is

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[1] *Chemist-Analyst*, 17, 3 (1928)

[2] Henry Bassett, *The Theory of Quantitative Analysis.*

advisable to add permanganate to the acid solution until a permanent pink color is obtained, in order to make sure that the iron is all in the ferric state before precipitating with cupferron.

4. Colorimetric Determination

Very small quantities of iron are best determined by measuring in a colorimeter or in Nessler tubes the depth of red color produced by ferric and thiocyanate ions. Schlesinger and Van Valkenburgh[1] think that the red color is due to the formation of the complex salt $Fe[Fe(CNS)_6]$. This view is substantiated by the facts that the molecular weight in ether or benzene corresponds to this formula and in electrolysis the complex $[Fe(CNS)_6]^{---}$ ion migrates toward the anode. Most of the facts, however, can be explained by the simpler assumption that undissociated $Fe(CNS)_3$ is formed. For the production of the color a considerable excess of thiocyanate is desirable, and the solution should be between 0.05 and 0 5 N in hydrochloric or nitric acid. Sulfate is preferably absent, except in small quantities, because sulfate ions have a tendency to form complexes with ferric ions.

Procedure. Prepare a standard solution containing 10 mg of Fe per liter. To do this take exactly 0.0100 g of pure iron wire, 0.0498 g of $FeSO_4 \cdot 7H_2O$, 0.0702 g of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, 0.0864 g of $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$, or 0.0902 g of $Fe_2(SO_4)_3 \cdot K_2SO_4 \cdot 6H_2O$, and dissolve in 20 ml of 3 N HCl. Dilute the solution somewhat and add 0.1 N KMnO$_4$ to the cold solution until a slight excess is shown by the pink color. This is to make sure that all the iron is in the ferric state. Transfer the solution to a liter volumetric flask, dilute to the mark, and mix by pouring back and forth at least 4 times into a large beaker which is dry at the start.

In each of several 50-ml Nessler tubes place 10 ml of N KCNS solution and an equal volume of 2 N HCl. To one of these add an aliquot part of the ferric chloride solution to be tested and water up to the mark. To another add the standard ferric chloride solution from a buret until the color matches that of the unknown solution. Then make up to 50 ml and add more of the standard if necessary. It is best to look down into the tubes, which should be placed against a white background.

The color comparison can also be made in a colorimeter. The results are accurate to about 2 per cent of the actual iron content, and the color comparison is best made with solutions containing between 0.04 and 0.1 mg Fe in 50 ml. It is possible to determine 0.001 to 1.0 mg of Fe in this way.

Determination of Iron and Sulfur in Ferrous Ammonium Sulfate

The determination of iron is one of the best known of all the gravimetric methods of analysis, and for many years it has been the custom to require most students of

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[1] *J. Am. Chem. Soc.*, **53**, 1212 (1931).

analytical chemistry in the colleges of the United States to carry out an analysis of ferrous sulfate or of ferrous ammonium sulfate. In a sulfate solution, some basic ferric sulfate is often formed if the precipitation of ferric hydroxide is accomplished by merely neutralizing with ammonia. It is the general practice, therefore, to dissolve the first precipitate in acid and repeat the precipitation with ammonia

It has been shown, however, that the formation of basic sulfate can be prevented if a considerable excess of ammonium hydroxide is used.

Procedure. Weigh out, to the nearest milligram, duplicate portions of 0.7–1.0 g into 400-ml beakers. Moisten the sample with 5 ml of 6 N hydrochloric acid, dilute with 5 ml of water, and heat, if necessary, to dissolve the sample. Heat nearly to boiling, and to the hot solution add concentrated nitric acid, drop by drop, until all the iron is oxidized to the ferric condition. When the iron is partially oxidized, the nitric oxide combines with the excess of ferrous salt, forming a dark brown, unstable compound. Continue adding the nitric acid until the dark color fades and a clear yellow solution is obtained. Not more than 2 ml of nitric acid should be necessary.[1] Boil gently for about 3 minutes to remove the reduced nitrous compounds. Dilute to about 200 ml and neutralize with ammonium hydroxide, finally adding 5–7 ml of concentrated ammonium hydroxide in excess. Heat carefully to about 70° and allow the precipitate to settle. Filter through a filter that has an ash of less than 0.1 mg, wash the precipitate twice by decantation with 50-ml portions of hot water, and finally with hot water from the wash bottle until free from chloride. Ignite slowly and carefully in an open porcelain or platinum crucible and weigh as Fe_2O_3. Report the percentage of iron present in the sample.

Dilute the filtrate to about 400 ml, neutralize with hydrochloric acid, and add 25 milli-equivalents in excess. Heat to boiling and precipitate the sulfate as described under "Sulfuric Acid" (Hintz and Weber).

TITANIUM, Ti. At. Wt. 47.90

Titanium occurs very commonly in rocks but usually only in small quantities. It occurs together with zirconium, cerium, and thorium and is very similar to zirconium in its chemical behavior.

For the determination of small quantities of titanium the colorimetric method is very satisfactory except when large quantities of iron, phosphorus, alkali salts, or even traces of vanadium are present. When

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[1] Bromine or hydrogen peroxide can be used instead of nitric acid. If a black iron precipitate is obtained later upon adding ammonium hydroxide, owing to incomplete oxidation, add 10 ml of 3 per cent hydrogen peroxide and heat till the precipitate is reddish brown.

these elements interfere it is not advisable to try the colorimetric determination until after they have been removed.

When titanium is unaccompanied by other cations of this group it is best to precipitate it with ammonia. The precipitate of $Ti(OH)_4$, or hydrated TiO_2, is not dissolved by an excess of ammonia and is easily converted into TiO_2 by ignition.

Usually it is necessary to remove titanium from interfering elements and then, after the separation has been accomplished, it is best to determine the titanium volumetrically or colorimetrically.

In Schoeller and Powell's method (cf. p. 222) titanium is precipitated as the red tannin adsorption complex from fairly acid oxalate solutions, which provides a quantitative separation from aluminum. The Gooch method depends upon adding alkali acetate and carrying out a basic acetate precipitation. The titanium precipitates in the presence of sufficient acetic acid to keep most of the aluminum in solution. The Baskerville method is based upon the fact that a nearly neutral solution of titanium and iron chlorides when boiled with sulfurous acid at moderate dilution gives a precipitate of titanium hydroxide while the iron remains in solution in the ferrous state. Thornton recommends the use of cupferron (ammonium nitrosophenylhydroxylamine). These methods will be discussed under the separations described a little farther on.

1. Determination as Titanium Dioxide

Precipitate with ammonia in the manner described under "Iron" (p. 153) or, to the nearly neutral solution, add 10 g of ammonium acetate and 10 ml of glacial acetic acid. Dilute to about 150 ml, heat to boiling, and filter. Wash the precipitate with 7 per cent acetic acid, ignite, and weigh as TiO_2.

Titanium is precipitated quantitatively by cupferron in dilute sulfuric acid. The solution can be as much as 14 N in sulfuric acid and can contain 1 per cent of tartaric acid. Ignition of the precipitate gives TiO_2. Aluminum, chromium, uranyl, nickel, alkaline earths, and phosphate do not interfere under suitable conditions. Iron, zirconium, columbium, tantalum, vanadium, certain rare earths, tungsten, copper, lead, silver, mercury, and bismuth are also precipitated by cupferron (cf. p. 154). The list of interfering elements is long, but several of them can be removed easily before precipitating with cupferron. Thus copper, lead, silver, mercury, and bismuth can be removed with hydrogen sulfide in the presence of acid, and iron can be removed as sulfide in an ammoniacal tartrate solution; the tartrate prevents the precipitation of iron, aluminum, titanium, etc., by ammonia. Titanium is almost always present to some extent in rocks but some of the other elements are rarely present. In working with solutions containing titanium, it is necessary to remember that titanium salts hydrolyze readily and, when once precipitated, the metatitanic acid, H_2TiO_3, or a basic titanium salt is very hard to dissolve again. Titanium phosphate is also hard

to dissolve in acid, and small quantities of titanium and phosphate are usually present with the silicic acid that separates when an acid solution is evaporated to dryness. To recover the titanium from the silica, it is simplest to volatilize the silica with sulfuric and hydrofluoric acids and fuse the residue with potassium pyrosulfate. In ordinary commercial work, the iron, aluminum, titanium, zirconium, etc., are commonly reported as " combined oxides," in which case the residue obtained after the removal of silica with hydrofluoric acid is considered part of the " combined oxides," and the hydroxide precipitate is ignited in the same platinum crucible that contains the residue from the silica determination and the weight of the originally empty crucible is deducted from the weight of the crucible plus " combined oxides." If, in an analysis, an attempt is made to dissolve titanium hydroxide from a paper filter, the paper should eventually be ignited in order to recover in the ash the titanium that invariably remains invisibly attached to the paper.

For the small quantities of titanium occurring in rocks containing no appreciable quantities of the typical titanium minerals such as ilmenite and rutile, the following colorimetric procedure is used. It is suitable for the analysis of titanium ores when a portion of the solution representing only about 0 01 g of ore is taken for the colorimetric comparison.

2. Determination of Titanium Colorimetrically.   Method of A. Weller[1]

(Suitable for small quantities of titanium)

This determination depends upon the fact that acid solutions of titanium sulfate are colored yellow to orange when treated with hydrogen peroxide; the yellow color increases with the amount of titanium present and is not altered by an excess of hydrogen peroxide On the other hand, inaccurate results are obtained in the presence of hydrofluoric acid (Hillebrand), consequently it is not permissible to use for this determination hydrogen peroxide which has been prepared from barium peroxide by means of fluosilicic acid.[2] The so-called Perhydrol is excellent though other commercial brands of hydrogen peroxide are satisfactory. The strength of the peroxide, which need not be above 3 per cent, should be determined approximately by titration with permanganate from time to time or error may result from deterioration of the reagent on standing. The oxidation with hydrogen peroxide should take place in solutions which are at least 1.8 N in H_2SO_4, and it is usually better to make the solution 3 6 N in this acid Iron, nickel, and cobalt interfere if present in sufficient quantities to color the solution; error caused by a little of these elements can be overcome by adding corresponding quantities to the standard solutions before the addition of hydrogen peroxide Chromic, vanadic, and molybdic acids and cerium interfere because they also form colored compounds with hydrogen peroxide. Sexivalent chromium and molybdenum and quinquevalent vanadium give color tests with hydrogen peroxide, but these elements can be removed by precipitating the titanium

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[1] Ber., 15, 2593 (1882).

[2] To test for fluorine: Add a slight excess of sodium carbonate to 50 ml of the reagent and heat to decompose the peroxide Filter if a precipitate forms, and add to the boiling solution an excess of calcium chloride. Filter and ignite the precipitate Add acetic acid till the calcium carbonate is dissolved, filter, wash, and ignite the residue gently Test with sulfuric acid to see if a gas is evolved which will etch glass, and with sulfuric acid and silica to see if a gas is evolved which makes a drop of water turbid.

in the presence of a little iron with sodium hydroxide. Cerium is not often present but can be removed as oxalate or fluoride. The bleaching action of considerable alkali salt is not serious in solutions which are 3.6 N in H_2SO_4. When large quantities of iron are present, the color can be removed by adding phosphoric acid, but as this also exerts a bleaching effect upon the titanium color the same quantity of phosphoric acid must then be added to the standards. Of all the elements that tend to bleach the color of the titanium peroxide, fluorine is the worst, and, in fact, this element can be determined by measuring its bleaching effect. Fluorine can be removed, however, by repeated evaporation with sulfuric acid in platinum, and so chemically pure potassium fluotitaanate, K_2TiF_6, is commonly used in preparing the standards.

Preparation of the Standard Titanium Solution. The standard solution can be prepared from pure K_2TiF_6, $K_2TiO(C_2O_4)_2 \cdot 2H_2O$, or TiO_2.

(a) From Potassium Fluotitanate, K_2TiF_6. The salt can be purified by recrystallizing from water. When dried at 105°, it contains one molecule of water of crystallization.

Weigh out 1.62 g of the pure salt into a platinum dish, add 50 ml of 18 N H_2SO_4, and evaporate until dense fumes of sulfuric acid are evolved. Cool, wash down the sides of the dish, and again evaporate till fumes of sulfuric acid escape freely. Cool, add sufficient sulfuric acid to make the final concentration at least 1.8 N, and then dilute to exactly 500 ml in a volumetric flask. The mixed solution will contain 1.00 mg TiO_2 per ml.

If desired, the concentration can be checked by gravimetric analysis. Pipet off 50 ml of the solution, dilute to about 200 ml, heat to boiling, and make slightly ammoniacal. Filter, ignite, and weigh the residual TiO_2.

(b) From Potassium Titanium Oxalate, $K_2TiO(C_2O_4) \cdot 2H_2O$. Weigh out 4.435 g of the pure salt, which can be purified if necessary by recrystallizing from water, together with about 8 g of ammonium sulfate into a small Kjeldahl flask. Add 50 ml of concentrated sulfuric acid, heat gradually up to the boiling point, and maintain this temperature for 10 minutes to remove all oxalate as CO and CO_2. Cool, carefully pour into about 700 ml of water, rinse out the flask, and dilute to exactly 1 l. This solution should contain the equivalent of 1.00 mg TiO_2 per ml. It can be tested as described under (a).

(c) From Pure Titanium Oxide, TiO_2. Fuse 0.5 g of pure TiO_2 with $K_2S_2O_7$ until a clear melt is obtained. Cool, add gradually 6 ml of concentrated sulfuric acid, cool, add water, and heat to boiling. Transfer to a 500-ml volumetric flask, make up to the mark, and mix by pouring back and forth into a beaker at least 4 times. This solution should contain 1.00 mg of TiO_2 per ml. It can be tested as described under (a).

Colorimetric Comparison. The colorimetric comparison is best made in a solution which contains the titanium as sulfate in the presence of sufficient sulfuric acid to make the solution at least 1.8 N in acid. The color comparison can be made in Nessler tubes or, more advantageously, in a colorimeter.

In making an analysis, take 5 ml of the standard solution, mix with sufficient hydrogen peroxide to oxidize it fully (1 or 2 ml of the 3 per cent reagent), and dilute with 1.8 N sulfuric acid to 50 ml in a measuring flask. Each milliliter of this diluted standard contains 0.1 mg of TiO_2.

It is most convenient in rock analysis to determine titanium in the solution which has been used for the titration of the total iron after fusing Al_2O_3, Fe_2O_3, etc., with $K_2S_2O_7$. For accurate work, however, correction should be made for the iron and alkali content.

If necessary, evaporate the sulfate solution containing the titanium to less than 100 ml. It should be at least 1.8 N in H_2SO_4. Add sufficient hydrogen peroxide to oxidize the titanium fully. Then, if the color is less than that of the standard, dilute to exactly 100 ml. If the color is deeper, dilute to 200 ml or until the shade is weaker than the standard. Using a colorimeter or Nessler tube, dilute 10 ml of the standard solution with 5 per cent sulfuric acid from a buret until, when viewed horizontally, the color matches that of the solution being analyzed. Repeat the comparison with several portions of the standard. Then, since the volume of the diluted standard and its titanium content are known, it is easy to compute the weight of TiO_2 per milliliter of the solution being analyzed. Thus if a ml of the standard (0.1 mg per ml) were diluted with b ml of acid to make it correspond to the color of the tested solution, of which the total volume was A ml, then $\dfrac{0.1a \times A}{a+b} =$ milligrams TiO_2 present.

To correct for iron, it is usually sufficient to assume that the coloring power of 0.1 g of Fe_2O_3 in 100 ml of 5 per cent sulfuric acid is about equal to 0.2 mg of TiO_2 in the same volume. It is more exact, however, to add to the standard a quantity of ferric alum solution that corresponds to the weight of iron in the sample. If A is the milliliters of the test solution used in a preliminary test, made as just described, a the milliliters of the standard used, b the milliliters of acid used, p the weight of Fe_2O_3 corresponding to the iron in A, and x the weight of iron (in terms of Fe_2O_3) which should be present in each milliliter of 5 per cent sulfuric acid used for diluting the standard, then since bx is the weight of Fe_2O_3 in $(a+b)$ ml of diluted standard and $\dfrac{p}{A}$ is the weight of Fe_2O_3 per milliliter of solution being tested, we have

$$\frac{p}{A} = \frac{bx}{a+b} \quad and \quad x = \frac{p(a+b)}{Ab}$$

To correct for the bleaching effect of alkali sulfate, a similar computation will show how much should be added to the 5 per cent sulfuric acid solution used in diluting the standard. In ordinary rock analysis, however, no correction need be applied for the alkali sulfate present if the TiO_2 content exceeds 0.02 g, when 6 g of potassium ~~... is weighed from the ... . Al_2O_3, Fe_2O_3, etc., and the ... is dissolved~~

If vanadium is present, precipitate the titanium (and vanadium) with ammonia and fuse with sodium carbonate. Sodium vanadate is formed, which dissolves in water. Sodium titanate is hydrolyzed and none of it dissolves in water. After extracting with water, therefore, fuse the residue with $K_2S_2O_7$ and dissolve the melt in 5 per cent sulfuric acid.

Considerable phosphoric acid has a bleaching effect, but the quantity present in rocks is too small to be serious. It is not advisable, however, to attempt to compensate the effect of ferric sulfate by adding phosphoric acid, although this practice has been recommended.

Direct Colorimetric Determination. Take 0.100 g of finely powdered titanium ore and fuse it with 10 g of $KHSO_4$ in a small porcelain dish of about 65-mm diameter at the top. To avoid loss by spattering, it is best to heat the $KHSO_4$ carefully by itself until all the hydrogen is removed as water and the residual $K_2S_2O_7$ forms a quiet melt. To the fused pyrosulfate, carefully add the weighed sample of ore and heat until a clear melt is obtained. The temperature should be raised slowly until fumes of sulfuric anhydride are evolved, but it is best not to convert the pyrosulfate entirely to K_2SO_4. Cool, carefully add 6 ml of concentrated sulfuric acid, and heat until the melt is dissolved. Cool, add about 100 ml of water, and boil. Transfer to a 500-ml flask, make up to the mark with $2 N H_2SO_4$, and mix by pouring back and forth several times into a beaker. One milliliter of the solution = 0.001 g of ore.

Take 25.00 ml of this solution, add 2 ml of 3 per cent hydrogen peroxide, and dilute to the mark with $1.8 N H_2SO_4$ in a 50-ml Nessler tube. In a similar Nessler tube take about 48 ml of $2 N H_2SO_4$ and 2 ml of 3 per cent H_2O_2. Add the standard from a buret until the color of the standard solution matches that of the unknown solution. The comparison can be made in a colorimeter to advantage.

In colorimetric comparison with Nessler tubes, greater depth of color is obtained when the solutions are viewed vertically against a white background; it makes very little difference how much liquid is in the tube. When viewed horizontally the color is fainter in proportion to the amount of dilution. As a general rule, small quantities are best determined by looking vertically into the tube, but with larger quantities of material it is advantageous to dilute the more deeply colored solution until a match is made when viewed horizontally; in this case the volumes of standard and of solution measured must be known precisely.

CHROMIUM, Cr.   At. Wt. 52.01

Forms: Chromic Oxide, Cr_2O_3; Barium Chromate, $BaCrO_4$

(a) *Chromic Compounds*

Determination as Chromic Oxide

1. *By Precipitation with Ammonia*[1]

If the chromium is present in solution as chromic compound it can be precipitated exactly as described under " Aluminum," by means of

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[1] Cf. C. Rothaug, *Z. anorg Chem.*, **84**, 165 (1914).

the slightest possible excess of ammonia[1] in the presence of considerable ammonium salts (or, better still, by the addition of freshly prepared ammonium sulfide solution to the boiling solution). Wash the precipitated Cr(OH)₃ with 2 per cent ammonium nitrate solution and ignite wet in a platinum crucible. Cool and weigh as Cr_2O_3. The results obtained are always a few tenths of a per cent too high on account of the formation of small amounts of chromic chromate. It is best, therefore, to heat the precipitate and allow it to cool in a stream of hydrogen. Use a Rose crucible and introduce hydrogen from a Kipp generator. Weigh as Cr_2O_3.

If phosphoric acid is present, it will be found in the precipitate. In this case fuse the dried precipitate in a nickel crucible with sodium carbonate and sodium peroxide, whereby sodium chromate and sodium phosphate are obtained. Determine the chromate volumetrically as described for the analysis of *chromite*.

2. By Precipitation with Potassium Iodide-Iodate Solution. Method of Stock and Massaciu[2]

Carry out the determination as with aluminum (cf. p. 149). Treat the slightly acid[3] solution, contained in a porcelain dish, with a mixture of potassium iodide and iodate, decolorize after a few minutes by means of sodium thiosulfate solution, treat with a little more iodide and iodate and then again with a few milliliters of sodium thiosulfate, and heat half an hour on the water bath. The flocculent precipitate of chromic hydroxide settles quickly. Filter, ignite in hydrogen, and weigh as Cr_2O_3.

3. By Precipitation with Ammonium Nitrite[4]

If the solution of the chromic salt is acid, neutralize with ammonia until a slight permanent precipitate is obtained. Dissolve this precipitate with a few drops of hydrochloric acid and add an excess of 6 per cent ammonium nitrite. Boil the liquid until all nitrous fumes have been expelled. By this means practically all the chromium will have

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[1] An excess of ammonia prevents the complete precipitation of the chromium hydroxide; the filtrate is then colored pink. In such cases the filtrate must be boiled until the excess of ammonia is expelled and all the chromium is precipitated.

[2] *Ber.*, 1901, 467

[3] If the solution is strongly acid, it is neutralized by the addition of pure KOH solution, drop by drop, until a faint permanent turbidity is obtained.

[4] E. Schirm, *Chem. Ztg*, 1909, 877. Cf p 150. According to Schoeller and Schrauth (*ibid*, 1909, 1287), iron, chromium, aluminum, and zinc can be precipitated by means of aniline.

been precipitated, but in order to throw down the last traces, add ammonia, drop by drop, until the odor of free ammonia barely persists in the solution. Allow the precipitate to settle while the beaker remains on the water bath, filter, wash with hot water, ignite wet in a platinum crucible in an atmosphere of hydrogen, and weigh as Cr_2O_3.

(b) Chromates

If the chromium is present in solution in the form of an alkali chromate, free from chloride and large amounts of sulfuric acid, it may be determined very accurately by precipitation with mercurous nitrate solution as mercurous chromate; on ignition the latter is changed to Cr_2O_3.

Procedure. To the neutral or weakly acid solution add a solution of pure mercurous nitrate; brown, basic mercurous chromate ($4Hg_2O \cdot 3CrO_3$) is formed. On heating to boiling, the precipitate becomes a beautiful, fiery red, being converted into the neutral salt Hg_2CrO_4. This red salt settles very quickly, and if the precipitation is complete the solution above the precipitate will be colorless. After cooling, filter the precipitate off, wash it thoroughly with water containing a little mercurous nitrate, dry, and separate from the filter as completely as possible. Burn the filter in a platinum spiral, and ignite the ash with the main portion of the precipitate, gently at first and finally strongly, in a platinum crucible under a hood with a good draft. Weigh the residue as Cr_2O_3.

The purity of the mercurous nitrate must be tested before it is used. Five grams of the salt should leave no residue after being ignited.

This excellent method for the determination of chromium unfortunately permits only a very limited application. If the solution contains any considerable amount of chloride, mercurous chloride will be precipitated with the mercurous chromate, which, although volatile on ignition, renders the precipitate too bulky and the method inaccurate.

If, therefore, it is necessary to determine chromium present as chromate in a solution containing chloride, two other methods are at our disposal. The chromate may be reduced by boiling with sulfurous acid (or by evaporating with concentrated hydrochloric acid and alcohol) and analyzed according to (a), or it may just as accurately, and much more conveniently, be determined by precipitating as barium chromate.

Determination as Barium Chromate

There are many ways in which chromium can be oxidized to chromate. In the analysis of chromium minerals, fusion with sodium peroxide is commonly resorted to, and usually the analysis is finished by determining the volume of ferrous sulfate

solution required to reduce the chromate or the volume of sodium thiosulfate required to react with the iodine liberated when chromate is reduced by hydriodic acid. These methods will be discussed under "Volumetric Analysis." In qualitative analysis the barium is usually identified by precipitation as barium chromate; this precipitate can be weighed and used for the determination of either barium or chromium. When the chromate solution has been prepared by fusion with sodium peroxide, the aqueous solution should be boiled until excess peroxide has been decomposed and then made acid with acetic acid. Chromium can also be weighed as $PbCrO_4$[1] or as $CrPO_4$.[2]

Procedure. To the boiling neutral solution, or one weakly acid with acetic acid, add a solution of barium acetate, drop by drop,[3] and, after standing for some time, filter through a Gooch crucible (without using very strong suction, as otherwise the filter will soon get stopped up and the solution will filter extremely slowly). Wash the precipitate with hot water till all soluble barium salt is removed, then with dilute alcohol and dry in the hot closet. Suspend the crucible in a larger one of porcelain by means of an asbestos ring (cf. p. 59) and heat, at first gently, and finally over the full flame of a good Bunsen burner. After 5 minutes remove the cover and continue heating until the precipitate appears a uniform yellow throughout. Cool in a desiccator and weigh as $BaCrO_4$.

Sometimes the precipitate appears green on the sides of the crucible owing to a slight reduction (by means of dust, traces of alcohol, etc.) of chromic acid to chromic oxide. The latter gradually takes on oxygen from the air during the long-continued heating of the open crucible, so that the green color gradually disappears.

If a g of chromate were taken for analysis, and the barium chromate precipitate weighed p g, then the amount of chromium present may be calculated as follows:

$$x = \frac{100Cr}{BaCrO_4} \cdot \frac{p}{a} = \text{per cent Cr}$$

Colorimetric Determination of Chromium

For determining extremely small quantities of chromium, a colorimetric test like that with hydrogen peroxide is extremely delicate but the reaction is so sensitive that it is seldom used, and, besides, the yellow color of chromate ions in slightly alkaline solution is sufficiently deep to permit the determination of small quantities of chromium. In rock analysis, the aqueous extract obtained after fusion with sodium

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[1] Beringer, *Textbook of Assaying.*

[2] Arnold and Hardy, *Chem. News*, 57, 153 (1888); Joseph and Rae, *J. Chem. Soc.*, 111, 196 (1917).

[3] If the barium acetate solution is added too quickly some of it will be carried down with the barium chromate, so that too high results will be obtained.

carbonate and a little potassium nitrate is usually employed and none of the common elements interfere. If considerable potassium nitrate is used and the fusion is made in a platinum crucible over the blast lamp or Méker burner, a yellow color of the aqueous extract may be caused by dissolved platinum. Fusions in platinum crucibles should not be made at such a high temperature and the quantity of nitrate used should never be large enough to attack the crucible. If the fusion is made with sodium peroxide, a little iron sometimes colors the filtrate but this can be avoided by digesting the melt with water on the steam bath for an hour or more before filtering. Sometimes a false color is obtained when sodium hydroxide solutions are filtered through paper, but this can be prevented by first washing the paper thoroughly with dilute sodium hydroxide or by filtering through an asbestos filter.

Procedure. Prepare a standard solution by dissolving 0.2555 g of pure K_2CrO_4 or 0.1935 g of pure $K_2Cr_2O_7$ in water and diluting to exactly 1 liter in a volumetric flask. One milliliter of either solution equals 0.1 mg Cr_2O_3 or 0.0684 g Cr. The color comparison can be made very easily as follows: Concentrate the aqueous solution of the melt to 50 ml or dilute the solution to some multiple of this volume and, after mixing, use a 50-ml aliquot part in a 50-ml Nessler tube. Into another similar cylinder put nearly as much water and 1 g of sodium carbonate. Add dropwise, with stirring, the standard solution of chromate until the two solutions show the same color when viewed from above against a white background. In making this test, the alkalinity of the standard and of the solution tested should be about the same. If uranium is present, the method fails because this element also gives a yellow-colored solution after fusion with an alkaline flux.

URANIUM, U.   At. Wt. 238.07

Forms: U_3O_8 and UO_2

Determination as U_3O_8

Uranium is usually precipitated by means of ammonia as ammonium uranate ($NH_4)_2U_2O_7$ and changed to U_3O_8 by gentle ignition in a platinum crucible with free access of air. The method is accurate if nothing else is present that will precipitate on neutralizing the solution and if care is taken to avoid the presence of CO_2; $(NH_4)_2U_2O_7$ dissolves in $(NH_4)_2CO_3$, forming $(NH_4)_4[UO_2(CO_3)_3]$. The precipitation with ammonia should be carried out as described for aluminum, and the ammonium uranate precipitate should be washed with hot 2 per cent ammonium nitrate solution.

According to the temperature of ignition, the U_3O_8 appears dirty green or black, and is difficultly soluble in dilute hydrochloric or sulfuric acids; in nitric acid it dissolves gradually. By heating with dilute sulfuric acid (1 vol. conc. $H_2SO_4 + 6$ vol. H_2O) in a closed tube at 150°-

175° for a long time (W. F. Hillebrand),[1] the U_3O_8 is completely dissolved with the formation of uranous and uranyl sulfates:

$$U_3O_8 + 4H_2SO_4 = 2UO_2(SO_4) + U(SO_4)_2 + 4H_2O$$
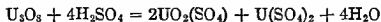
U_3O_8 is also readily soluble in dilute sulfuric acid in the presence of potassium bichromate. These two last facts are taken advantage of in the volumetric determination of uranium (which see).

If the ammonium uranate precipitate is heated over a Méker burner, or blast lamp, in a stream of hydrogen, it is converted into UO_2. This method also gives accurate results.

Precipitation from a Solution Containing Cupferron

Cupferron, $C_6H_5N\cdot NO\cdot ONH_4$, which is the ammonium salt of phenylnitrosobydroxylamine, is a valuable reagent because it precipitates iron, vanadium, zirconium, titanium, tin, columbium, and tantalum in strongly acid solutions. Uranium in uranyl salts, in which the valence of the uranium is 6, is not precipitated by cupferron so that a separation from ferric iron can be accomplished; but if, after the iron precipitate has been removed, the uranium is reduced to the quadrivalent state, all the uranium can be precipitated by means of cupferron, and the precipitate is converted into U_3O_8 by strong ignition.

Procedure. Evaporate the filtrate from the iron determination (cf. p. 155) to about 50 ml; add 20 ml of concentrated HNO_3 and 10 ml of concentrated H_2SO_4 if not already present. Evaporate until fumes of sulfuric acid are evolved freely, cool, add 20 ml more of HNO_3, and repeat the evaporation to fumes. Continue this treatment with nitric acid until all the organic matter present is oxidized as shown by no dark color appearing on evaporating. Then, to remove the last traces of nitric acid, allow the fuming solution to cool, wash down the sides of the beaker, and again evaporate to strong fumes. Cool, dilute to make the solution contain about 6 ml of concentrated sulfuric acid per 100 ml, and pass through a Jones reductor (see Index). Rinse out the reductor with 8 per cent sulfuric acid. Cool the reduced solution to below 15°; add macerated filter paper (p. 151) and an excess of 6 per cent cupferron solution. Filter and wash with cold 4 per cent H_2SO_4 solution containing 1.5 g of cupferron per liter. Ignite and weigh as U_3O_8.

SEPARATION OF IRON, ALUMINUM, CHROMIUM, TITANIUM, AND URANIUM, FROM CALCIUM, STRONTIUM, BARIUM, AND MAGNESIUM

To the solution containing the above substances in the presence of considerable ammonium chloride in an Erlenmeyer flask, add a slight excess of freshly prepared ammonium sulfide, free from sulfate and

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[1] *Bull. U. S. Geol. Survey*, 78, p. 90.

carbonate. After standing over night filter off the precipitate and wash it with water containing ammonium sulfide. It contains the iron and uranium as sulfides, the aluminum, chromium, and titanium as hydroxides. If large amounts of magnesium are present, some of it is almost always present in the precipitate, so that it is then necessary, after filtration, to dissolve the precipitate in hydrochloric acid and to reprecipitate with ammonium sulfide.

Instead of using ammonium sulfide, the separation can be accomplished satisfactorily with ammonia; the iron must then be in the ferric condition. Carry out the treatment as described for the precipitation of aluminum with ammonium hydroxide using methyl red as indicator.

Separation of Iron from Aluminum

1. To a boiling solution of half-normal sodium hydroxide in a porcelain dish, add the dilute acid solution of ferric and aluminum chlorides. After the solutions are all mixed make sure that an excess of alkali hydroxide is present so that all the iron is precipitated as $Fe(OH)_3$[1] and all the aluminum dissolved as $NaAlO_2$. Dilute with hot water and filter. For the iron determination, dissolve the precipitate in hydrochloric acid, reprecipitate with ammonia,[2] dry and weigh as Fe_2O_3 (see p. 153). Precipitate the aluminum as hydroxide in the filtrate by acidifying with nitric acid and then adding ammonia. Filter, wash with 2 per cent ammonium nitrate solution, and weigh as Al_2O_3.

2. Add three times as much tartaric acid as corresponds to the weight of dissolved Fe_2O_3 and Al_2O_3 and pass hydrogen sulfide into the solution until it is saturated. Add a very slight excess of ammonia, and allow the sulfide of iron to settle in a closed Erlenmeyer flask. Filter, wash with water containing ammonium sulfide, dissolve in hydrochloric acid, oxidize with a little potassium chlorate or nitric acid, and precipitate as ferric hydroxide by the addition of ammonia. Determine the aluminum in the filtrate by evaporating to dryness with the addition of a little sodium carbonate and potassium nitrate.[3] Gently ignite the residue in a platinum dish to destroy the tartaric acid, dissolve the residue in dilute nitric acid, filter off the carbon, and precipitate the aluminum from the solution by the addition of ammonia.

[1] If the precipitate is large, it should be dissolved in hydrochloric acid and again precipitated with NaOH.

[2] It is very hard to wash the NaOH precipitate free from alkali so that the first precipitate should not be weighed.

[3] For the direct determination of aluminum by precipitation with tannin and without destroying tartaric acid, see p. 222.

3. Add sodium carbonate solution to the neutral solution of the chlorides or sulfates (not the nitrates) until a slight permanent precipitate is formed; dissolve this by the addition of a few drops of hydrochloric acid. Dilute the solution to about 250 ml for each 0.1 or 0.2 g of the metals present, add an excess of sodium thiosulfate solution, and boil the solution until every trace of SO_2 has disappeared. By this operation the ferric salt is reduced to ferrous salt:

$$2Na_2S_2O_3 + 2FeCl_3 = 2NaCl + Na_2S_4O_6 + 2FeCl_2$$

and the aluminum is precipitated as the hydroxide:

$$2AlCl_3 + 3H_2O + 3Na_2S_2O_3 = 6NaCl + 3SO_2 \uparrow + 3S + 2Al(OH)_3$$
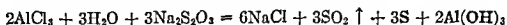
Filter off the precipitate of aluminum hydroxide and sulfur, wash with hot water, dry, transfer as completely as possible to a porcelain crucible, burn the filter in a platinum spiral and add the ash to the crucible. Ignite gently until all the sulfur has been expelled and then more strongly over the blast or Méker burner until the weight is constant. Cf. p. 149.

To determine the iron, make the filtrate acid with hydrochloric acid, boil off the SO_2, filter off the sulfur, oxidize the solution with nitric acid, and precipitate the iron as ferric hydroxide as described on p. 153.

Or add ammonia and ammonium sulfide to the filtrate from the $Al(OH)_3$ precipitate, filter, and wash with hot water. Dissolve the iron sulfide in hot 2 N hydrochloric acid, oxidize to the ferric condition with concentrated nitric acid, dilute, and precipitate with ammonia according to p. 153.

4. Precipitate both iron and aluminum with ammonia, filter, wash, dry, ignite in a porcelain or platinum crucible, and determine the weight of the combined oxides. After a constant weight is obtained, digest the mixed oxides with concentrated hydrochloric acid to which a little water has been added ($10HCl : 1H_2O$) in a covered crucible until the iron is completely dissolved. If ferric oxide predominates, as it frequently does, the solution is effected in 1 or 2 hours. If, on the other hand, a relatively large amount of alumina is present, as is usual with silicates, a condition which can be predicted by the color of the precipitate produced by ammonia, the precipitate dissolves very slowly and many times only incompletely.

In the latter case instead of treating with hydrochloric acid, fuse the ignited oxides with 12–15 times as much potassium pyrosulfate, $K_2S_2O_7$ (cf. Vol. I).[1] The conversion of the oxides into sulfates is

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[1] E. Deussen finds that fusion with KF·HF works better. The platinum is not attacked and the solution is effected more readily. *Z. angew. Chem.*, 1905, 815.

usually complete in 2–4 hours.[1] Place the crucible together with its cover in a beaker, add water and a little sulfuric acid, and dissolve the melt by warming gently and passing a current of air through the solution in order to keep the liquid in motion. A small amount of platinum is always dissolved by this treatment.[2] After removing the crucible and its cover, heat the solution to boiling and reduce with hydrogen sulfide as described in Chapter XV. After the iron is reduced, filter off the platinum sulfide, again introduce hydrogen sulfide, and continue as described in Chapter XV, finally titrating the reduced iron with standard potassium permanganate in 250 ml of cold acid solution. The aluminum is determined from the weight of the combined oxides after deducting the weight of Fe_2O_3 corresponding to the volume of permanganate used in the titration.

For the determination of iron in silicates the above process is most suitable (Hillebrand). The reduction of the ferric salt to ferrous salt by means of hydrogen sulfide possesses advantages over the reduction by means of zinc, for in the former case no foreign element is introduced, and furthermore zinc serves to reduce the titanium that is almost always present in rocks, and this will be again oxidized by the permanganate, so that too high an iron value will be obtained. When titanium is present, it is better to reduce with sulfurous acid as described in Chapter XV of this book.
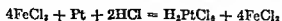
If all the iron is dissolved by treating the oxides with hydrochloric acid, evaporate the solution to dryness and treat the residue with a few milliliters of dilute sulfuric acid, evaporate on the water bath as far as possible, and then heat over the free flame until fumes of sulfuric acid are evolved. After cooling, dissolve the sulfates in water and reduce the ferric sulfate to ferrous sulfate by introducing a piece of zinc, free from iron, into the crucible and covering with a watch glass. The reduction is complete in 20–30 minutes. Filter off the slight residue of platinum[3] with the excess of zinc, catching the filtrate in a flask already filled with carbon dioxide. Wash the residue with water that has been boiled, and titrate the solution with potassium permanganate solution.

This method is to be recommended for the determination of small

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[1] If the precipitate produced by ammonia is well mixed with filter-paper pulp (cf. p. 151) the ignited oxides will be obtained in a condition such that the fusion with potassium pyrosulfate can be made within 10 minutes.

[2] If the fusion is made in a silica crucible, there will be no platinum to remove.

[3] Platinum is perceptibly attacked by long digestion with ferric chloride solution:

$$4FeCl_3 + Pt + 2HCl \rightleftharpoons H_2PtCl_6 + 4FeCl_2$$

The chloroplatinic acid is reduced to platinum by the action of zinc.

amounts of iron in the presence of still less aluminum, as in the analysis of mineral waters.

The following procedure leads to the same end, but the results are not quite so reliable:

Dilute the solution in which the iron and aluminum are to be determined to a definite volume (e.g., 250 ml) and take two aliquot portions by means of a pipet (usually 100 ml).

In one portion determine the weight of the combined oxides of iron and aluminum by precipitation with ammonia and ignition of the precipitate as described on p. 148; in the other aliquot determine the iron by titration. If the solution contains hydrochloric acid, as is usual, it is best first to precipitate the iron with ammonia, filter, wash, and dissolve in dilute sulfuric acid. Reduce this solution and titrate as described above.[1]

Separation of Iron, Aluminum, and Phosphoric Acid

Although the determination of phosphoric acid has not yet been described, its determination in the presence of iron and aluminum will now be discussed because this highly important separation is necessary in the analysis of almost all minerals containing iron and aluminum as well as in the analysis of many mineral waters. Two cases are to be distinguished:

1. The solution contains only a small amount (a few centigrams or less) of iron, aluminum, and phosphoric acid.

2. The solution contains large amounts of these substances.

1. In the first case the determination of all three constituents must be undertaken in the same portion, as otherwise errors would be introduced on account of the small quantities to be determined. First treat with ammonia as described on p. 148 whereby the iron, aluminum, and phosphoric acid are precipitated.[2]

Ignite the precipitate in a platinum crucible and weigh:

$$Fe_2O_3 + Al_2O_3 + P_2O_5 = A$$

Fuse the oxides with 6 times their weight of a mixture consisting of 4 parts anhydrous sodium carbonate and 1 part pure silica. Heat

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[1] It is desirable to get rid of the hydrochloric acid on account of its action upon potassium permanganate (cf. Chapter XV). In the presence of hydrochloric acid, the Zimmermann-Reinhardt method of reducing with stannous chloride and titrating with permanganate is capable of giving good results. See Chapter XV.

[2] The phosphoric acid is usually present in such small amounts that the iron and aluminum are more than sufficient to effect the precipitation of all the phosphoric acid, on the addition of ammonia, as phosphates of these metals.

usually complete in 2–4 hours.[1] Place the crucible together with its cover in a beaker, add water and a little sulfuric acid, and dissolve the melt by warming gently and passing a current of air through the solution in order to keep the liquid in motion. A small amount of platinum is always dissolved by this treatment.[2] After removing the crucible and its cover, heat the solution to boiling and reduce with hydrogen sulfide as described in Chapter XV. After the iron is reduced, filter off the platinum sulfide, again introduce hydrogen sulfide, and continue as described in Chapter XV, finally titrating the reduced iron with standard potassium permanganate in 250 ml of cold acid solution. The aluminum is determined from the weight of the combined oxides after deducting the weight of Fe_2O_3 corresponding to the volume of permanganate used in the titration.

For the determination of iron in silicates the above process is most suitable (Hillebrand). The reduction of the ferric salt to ferrous salt by means of hydrogen sulfide possesses advantages over the reduction by means of zinc, for in the former case no foreign element is introduced, and furthermore zinc serves to reduce the titanium that is almost always present in rocks, and this will be again oxidized by the permanganate, so that too high an iron value will be obtained. When titanium is present, it is better to reduce with sulfurous acid as described in Chapter XV of this book.

If all the iron is dissolved by treating the oxides with hydrochloric acid, evaporate the solution to dryness and treat the residue with a few milliliters of dilute sulfuric acid, evaporate on the water bath as far as possible, and then heat over the free flame until fumes of sulfuric acid are evolved. After cooling, dissolve the sulfates in water and reduce the ferric sulfate to ferrous sulfate by introducing a piece of zinc, free from iron, into the crucible and covering with a watch glass. The reduction is complete in 20–30 minutes. Filter off the slight residue of platinum[3] with the excess of zinc, catching the filtrate in a flask already filled with carbon dioxide. Wash the residue with water that has been boiled, and titrate the solution with potassium permanganate solution.

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In one portion determine the weight of the combined oxides of iron and aluminum by precipitation with ammonia and ignition of the precipitate as described on p. 148; in the other aliquot determine the iron by titration. If the solution contains hydrochloric acid, as is usual, it is best first to precipitate the iron with ammonia, filter, wash, and dissolve in dilute sulfuric acid. Reduce this solution and titrate as described above.[1]

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Ignite the precipitate in a platinum crucible and weigh:

$$Fe_2O_3 + Al_2O_3 + P_2O_5 = A$$

Fuse the oxides with 6 times their weight of a mixture consisting of 4 parts anhydrous sodium carbonate and 1 part pure silica. Heat

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[2] The phosphoric acid is usually present in such small amounts that the iron and aluminum are more than sufficient to effect the precipitation of all the phosphoric acid, on the addition of ammonia, as phosphates of these metals.

the mixture over the blast lamp or Méker burner. Cool, extract the melt with water to which a little ammonium carbonate has been added, and filter. The filtrate contains all the phosphoric acid and a very little silicic acid; the residue contains all the iron and aluminum and considerable silica.

For the determination of the phosphoric acid, evaporate the filtrate to dryness with hydrochloric acid on the water bath in order to remove the silica, moisten the residue with 6 N hydrochloric acid, take up in a little water, filter, and precipitate the phosphoric acid in the filtrate by the addition of ammonia and "magnesia mixture," as described under "Phosphoric Acid." By igniting in a porcelain crucible change the precipitate of magnesium ammonium phosphate to magnesium pyrophosphate, and from its weight p calculate the amount of phosphoric anhydride, P_2O_5 ($= B$):

$$B = \frac{P_2O_5}{Mg_2P_2O_7} \cdot p$$

Subtract B and A to get the combined weight of the iron and aluminum oxides and then after determining the iron by titration the aluminum can be estimated "by difference." For the determination of the iron, take the insoluble residue obtained after treating the product of the fusion with water and ammonium carbonate and digest it with hydrochloric acid in a small porcelain crucible until the iron oxide is completely dissolved. Add a little 18 N sulfuric acid, and evaporate first on the water bath and then over a free flame until fumes of sulfuric anhydride are evolved. After cooling, add water and digest on the water bath for some time. Filter off the silica, reduce the solution by means of hydrogen sulfide (cf. p. 169, sub. 4), and, after removing the excess of hydrogen sulfide, titrate the iron with permanganate solution.[1] From the amount of permanganate used, the quantity of ferric oxide (C) can be calculated, and by deducting this from the weight of the combined oxides the weight of the Al_2O_3 is ascertained:

$$A - (B + C) = Al_2O_3$$

2. If the solution contains large amounts of iron, aluminum, and phosphoric acid, divide it into three aliquot portions and in one determine the value of A by precipitation with ammonia; in the second determine the phosphoric acid by the molybdate method as described under "Phosphoric Acid"; and in the third determine the iron by titration.

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[1] Instead of reducing the iron, the ferric salt may be titrated directly with titanous chloride or iodimetrically (see Chapter XV).

Separation of Iron from Chromium

1. The chromium is oxidized in alkaline solution by means of chlorine, bromine, or sodium peroxide to a soluble chromate, and the insoluble ferric hydroxide is filtered off. If the chromium alone is desired, it is often better to fuse with sodium carbonate and peroxide as described for the analysis of chromite.

Procedure. Pour the solution of the chlorides into an Erlenmeyer flask of Jena glass, provided with a ground-glass stopper and tubes by which gas may enter and leave the flask, and add sodium hydroxide solution until strongly alkaline. Heat on the water bath and conduct chlorine gas through the liquid, or add bromine water, until it becomes distinctly yellow and the ferric hydroxide has assumed its characteristic reddish brown color. When the oxidation is accomplished by chlorine gas, the equivalent of 0.5 g of the mixed oxides will be completely oxidized in 15 to 20 minutes. Instead of chlorine or bromine, sodium peroxide is often more convenient for converting Cr^{+++} into CrO_4^{--}. In this case, add the peroxide in small portions to the *cold* solution. After the oxidation is complete heat the solution until the excess peroxide is decomposed into NaOH and O_2.

Carefully make the filtrate acid with acetic acid, precipitate the chromium by the addition of barium acetate, and treat the precipitate of barium chromate as described on p. 165. Dissolve the ferric hydroxide in hydrochloric acid, reprecipitate with ammonia as described on p. 153, and weigh as ferric oxide.

Remark. If the chromate is to be determined as barium chromate, the solution must contain no sulfuric acid. If sulfuric acid is present, reduce the chromate by evaporating with hydrochloric acid and alcohol. In the solution of chromic chloride thus obtained determine the chromium as chromic oxide after precipitation with ammonia as described on p. 163.

In the case of a precipitate containing iron and chromic oxides, fuse with sodium carbonate and a little potassium chlorate. Extract the melt with water, and determine the chromium in the aqueous solution by precipitating with barium acetate as described on p 165. Dissolve the residue from the aqueous extraction of the fusion in hydrochloric acid, precipitate with ammonia, and determine the iron as f . . . . p 153.

. .   . . .

nitrate, extract the melt with water, neutralize the solution with nitric acid, and precipitate with mercurous nitrate solution, as described on p 164.

2. It has been proposed that the mixture of ferric and chromic oxides be analyzed by strongly igniting in a stream of hydrogen so that the ferric oxide is reduced to metallic iron while the chromic oxide is unchanged. The iron could then be determined by the loss of weight. Experiments show, however, that the ferric oxide is often so enveloped

in chromic oxide that it is not even approximately reduced even when heated over the blast lamp.

3. Iron may be separated from chromium by precipitating the iron with ammonium sulfide from a solution containing sufficient ammonium tartrate to prevent the precipitation of the chromium. The separation is the same as was described under "Aluminum," p. 168, sub. 2.

Separation of Aluminum from Chromium

If the chromium is present as chromic salt, oxidize it to chromate by means of chlorine, bromine, or sodium peroxide as described on p. 173. Make acid with nitric acid, and determine the aluminum as oxide after precipitating with ammonia as described on p. 148. In the absence of sulfuric acid the chromium can be determined in the filtrate as barium chromate (cf. p. 165). If sulfuric acid is present, reduce the chromate to chromic salt by the action of concentrated hydrochloric acid and alcohol, precipitate with ammonia, and weigh as the oxide (see p. 163).

If, however, the chromium is already present as chromate, at once precipitate the aluminum, with ammonia as hydroxide, as described on p. 148.

Separation of Iron from Titanium

It is frequently necessary to determine both iron and titanium in a precipitate produced by ammonia consisting of a mixture of these two oxides alone, but it is more often necessary to determine titanium in the presence of iron, aluminum, and phosphoric acid, all of which are precipitated by ammonia in the analysis of rocks.

For the separation of titanium from iron in the absence of alumina, the following methods are suitable:

1. Ignite the precipitate produced by ammonia and weigh the mixture of oxides. Fuse it in a silica crucible with 15–20 times as much potassium pyrosulfate. Before starting the fusion, heat the pyrosulfate, or fused potassium acid sulfate, in a silica crucible until it begins to evolve fumes of sulfuric anhydride. Fuse the oxides with this dehydrated pyrosulfate until they are converted to sulfates. Use a small flame and heat so that only a slight fuming is noticed when the crucible cover is raised. As the fusion progresses the color of the melt darkens, and the melting point of the mass rises as the sulfuric anhydride escapes. When the fusion is finished, there should be no unattacked oxide visible in the melt. If the temperature is raised too quickly, sulfuric acid escapes without reacting with the oxide, and if all the pyrosulfate is converted to sulfate, the mass expands on cooling and may crack the crucible. It is a good plan to add a little pyrosulfate at the

last to prevent this or to add a little concentrated sulfuric acid to the solidified melt and then beat again. If the pyrosulfate is not anhydrous, the escaping steam will carry up some of the oxides to the top of the crucible and spatter them on the cover, and these particles are likely to escape the action of the pyrosulfate.

When the fusion is finished, make a spiral at the end of a 4-inch piece of platinum wire and insert this spiral in the melt. Let the contents of the crucible solidify and become cold. Then remove the melt by heating the sides of the crucible and pulling on the wire while holding the crucible with tongs. Suspend the melt from a stirring rod which rests on the top of a beaker containing *cold* 0.5 N sulfuric acid. Stir mechanically to hasten the dissolving. If necessary, filter off any undecomposed oxide. Treat this with sulfuric and hydrofluoric acids to make sure that no silica is present and again fuse with pyrosulfate. Dissolve any residue in the crucible with dilute sulfuric acid.

For the iron determination, it is best to reduce it to the ferrous state and titrate with permanganate. If hydrogen sulfide is used as the reducing agent (p. 542) the titanium is unaffected but if a Jones reductor is used (pp. 543–4), which is somewhat more convenient, the quadrivalent titanium is reduced to the trivalent state. If the air in the reductor flask is replaced by CO_2, both iron and titanium can be oxidized by permanganate. If, however, air is bubbled through the solution at room temperature until the purple color of Ti^{+++} disappears and for 5 minutes longer, all the Ti^{+++} is oxidized by the air and only an inappreciable quantity of Fe^{++}, so that now the iron can be titrated alone. Three procedures are to be recommended:

(a) Reduce the solution with a Jones reductor, aerate to oxidize the titanium and titrate with permanganate. Then, if the titanium content is small, determine the titanium colorimetrically (p. 159) in an aliquot part of the solution.

(b) Make up the solution to a definite volume, mix and use an aliquot part for the iron determination as in (a) and in another aliquot determine both iron and titanium by permanganate titration under an atmosphere of CO_2.

(c) Determine the iron as in (a) and in another aliquot determine the titanium gravimetrically as TiO_2. Neutralize the solution with sodium carbonate until a very slight permanent turbidity is produced in the well-stirred solution. Add an excess of sodium thiosulfate and continue as described on page 169.

Separation of Aluminum from Titanium

One of the best methods of separation is that of Gooch;[1] it consists in boiling a solution of the two elements containing considerable free acetic acid and alkali acetate; by this means all the titanium and little, if any, of the aluminum present is precipitated. If, however, the amount of aluminum present is large (as is usual in rock analysis), the separation must be repeated. There is never any danger of the precipitation of the titanium being incomplete.

In practice it is almost always necessary to separate the titanium not from aluminum alone, but from iron and aluminum, so that the method of Gooch will be described for this more general case.

Treat the solution obtained by dissolving the pyrosulfate melt in *cold* dilute acid[2] with three times as much tartaric acid as the weight of the oxides, saturate with hydrogen sulfide gas, and make slightly ammoniacal. By this means all the iron is precipitated as ferric sulfide, while the aluminum and titanium remain in solution. Filter off the iron sulfide, acidify the filtrate with sulfuric acid, heat to boiling, and filter off the precipitate of sulfur and platinum sulfide (the latter from the platinum crucible in which the fusion with pyrosulfate was made). Boil the filtrate to expel the last traces of hydrogen sulfide, and destroy the tartaric acid by adding $2\frac{1}{2}$ times as much potassium permanganate as there is tartaric acid present. Add sulfurous acid until the precipitated manganese dioxide is redissolved, after which add a slight excess of ammonia and 7–10 ml of glacial acetic acid for each 100 ml of solution. Boil the solution for 1 minute, allow the precipitate to settle, and decant the filtrate through a filter.[3] Finally transfer the precipitate to the filter, and wash with 7 per cent acetic acid and finally with a little hot water. Ignite the precipitate and weigh as TiO_2.

The precipitate contains manganese and aluminum; it must be purified. Fuse it with three times as much sodium carbonate. Leach the melt (colored green by the manganese) with cold water, leaving sodium metatitanate[4] and some alumina undissolved. Filter off the precipitate by means of a small filter, ignite this residue in a platinum crucible, and fuse again with alkali pyrosulfate. After cooling, dissolve the contents of the crucible in 200 ml of 0.1 N sulfuric acid. Add 5 g of sodium acetate and 20 ml of glacial acetic acid. After boiling

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[1] *Chem. News*, **52**, 55 and 68.

[2] See p. 175.

[3] Schleicher & Schüll's filter-paper No 589 is satisfactory for this purpose.

[4] The sodium metatitanate undergoes hydrolysis and forms a precipitate containing a much higher percentage of TiO_2.

1 minute and allowing to stand until settled, filter the precipitate, wash with 7 per cent acetic acid, then with water, dry, ignite, and weigh. This precipitate sometimes contains aluminum. Fuse it again with sodium carbonate and treat the melt with sulfuric acid, etc., exactly as described above. This time the precipitate is usually free from aluminum, but the process should be repeated until a constant weight is obtained.

This analysis does not require much time if the quantity of titanium present is so small that the precipitates filter and wash quickly.

For the determination of very small amounts of titanium, it is advisable to use the colorimetric method proposed by Weller (cf. p. 159).

The above method of Gooch is tedious and fails to take into consideration the fact that zirconium, if present, precipitates with titanium. Phosphoric and vanadic acids are also likely to precipitate with titanium and zirconium, but these were removed by the fusion with sodium carbonate which forms water-soluble sodium vanadate and phosphate. The titanium precipitate is also likely to contain some adsorbed alkali ions, but this error is slight in rock analysis. Thorium and cerium are also precipitated to some extent, but usually these elements are present to such a slight extent that they may be neglected. For the separation of titanium from aluminum, zirconium, and thorium by means of tannin, see p. 223. To obviate the necessity of destroying the tartaric acid in the method of Gooch, W. F. Hillebrand[1] recommends the following procedure:

Cupferron Method of Precipitating Titanium and Zirconium[2]

To the filtrate from the iron sulfide precipitate, which was formed in an ammoniacal ammonium tartrate solution to prevent the precipitation of aluminum, titanium, and zirconium by ammonia (cf. p. 176), add 40 ml of 18 N sulfuric acid and boil to expel the excess of hydrogen sulfide. Cool to 15°, or below, dilute to 400 ml, and add a cold 6 per cent solution of cupferron, with constant stirring (cf. p. 155). Allow the precipitate to settle and test the supernatant solution to see if the precipitation is complete; if so, a white turbidity forms instead of a yellow precipitate. Filter and wash 20 times with cold 1.2 N hydrochloric acid. Place the precipitate and filter in a crucible and dry at 110–120°. Then ignite very cautiously with a small flame placed at the base of the

[1] *Analysis of Silicate and Carbonate Rocks*, p. 166, 1919.
[2] W. M. Thornton, *Am. J Sci* [4], **37**, 407 (1914); *Chem. News*, **110**, 5 (1914); *Z. anorg Chem*, **87**, 375 (1914); Schroeder, *Z anorg Chem.*, **72**, 95 (1911); Thornton and Hayden, *Am. J. Sci.* [4], **38**, 137 (1914); *Chem. News*, **110**, 153 (1914); *Z. anorg Chem*, **89**, 377 (1914); Lundell and Knowles, *J. Am. Chem. Soc.*, **41**, 1801 (1919).

inclined, partly covered crucible. There is likely to be a sudden gush of smoke when the oxidation of the organic matter starts. Gradually raise the temperature until all the organic material is destroyed. Fuse the residue with sodium carbonate, extract the melt with water, filter, and wash with dilute sodium carbonate solution. Dissolve the residue in dilute sulfuric acid and repeat the precipitation with cupferron. Ignite and weigh as TiO_2 and ZrO_2. The separation of titanium and zirconium will be discussed on p. 181.

The Determination of Titanium in Titanium-Iron Ore

Method of Barneby and Isham[1]

The method of Barneby and Isham is based on the volatilization of the silica by hydrofluoric acid in the presence of sulfuric acid, evaporation to dryness, and fusion with sodium carbonate and a little potassium nitrate (which converts the iron and titanium to insoluble ferric oxide and sodium titanate), extraction with hot water to remove the soluble phosphates, sulfates, and aluminates, solution of the ferric oxide and sodium titanate in hydrochloric acid, extraction of ferric chloride with ether, reduction of slight traces of iron with sulfurous acid, precipitation of the titanic acid by boiling in acetic acid solution, filtration, and ignition to titanium oxide (or the titanium may be determined colorimetrically). The method is accurate except that it fails to take into consideration the probable presence of zirconium and other rare earths which will precipitate with the titanium more or less completely.

Procedure. Weigh out about 0.5 g of ore into a platinum crucible, moisten with a little water, and add 5 to 10 drops of concentrated sulfuric acid and about 2 ml of hydrofluoric acid. Heat the mixture carefully until finally no more sulfuric acid fumes are evolved. Add 5–10 g of sodium carbonate and a *little* potassium nitrate,[2] and fuse the mixture at least 30 minutes. Cool, place the crucible and cover in a beaker, add about 25 ml of hot water, and heat until the melt is disintegrated. Ferric oxide and sodium titanate are left insoluble in hot water. Remove the crucible, and dissolve any adhering particles of ferric oxide and hydrolyzed sodium titanate in hot 6 N hydrochloric acid; save this solution. Filter off the residue in the beaker and wash with hot water.[3] Perforate the filter and carefully wash the residue into a clean beaker with 6 N hydrochloric acid. (No water is to be added from this stage

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[1] *J. Am. Chem. Soc*, **32**, 957 (1910).

[2] The potassium nitrate is added to make sure that the crucible is not injured by any sulfide or reducible metal which may be present. Too much nitrate should not be added; it will injure the crucible and also cause the melt to effervesce badly.

[3] The residue should not be washed with too much hot water; the hydrolysis of the sodium titanate may go so far that the residue will not dissolve in hydrochloric acid.

of the analysis until after the subsequent treatment with ether.)   Transfer the hydrochloric acid washings from the platinum crucible to the beaker and then heat on the hot plate until complete solution has been effected and the total volume has been reduced to 15 or 20 ml.   Cool, add 2 ml of 12 N hydrochloric acid, and transfer the solution to a separatory funnel, rinsing the beaker with 6 N hydrochloric acid, d 1.10.   Add an equal volume of ether, which has been saturated with concentrated hydrochloric acid solution, to the solution in the funnel, insert a rubber stopper in the top, invert the funnel, open the stopcock, and shake thoroughly.   Close the stopcock, place the separatory funnel in an upright position, and allow to stand 10 minutes.   Then drain off the aqueous layer into a second separatory funnel.   Rinse the ether layer twice by shaking well with 5- to 10-ml portions of 6 N hydrochloric acid, and add the washings to the aqueous solution.   Repeat the treatment with ether two or three times until the last portion of ether fails to show any greenish tinge due to the presence of dissolved ferric chloride.

Rothe,[1] who first made use in quantitative analysis of the fact that ferric chloride dissolved in hydrochloric acid, d 1.1, can be removed by shaking with ether, recommended the double separatory funnel shown in Fig. 38, but an ordinary 125-ml single separatory funnel can be used satisfactorily.

Carefully heat the aqueous solution containing all the titanium in the presence of little, if any, iron and aluminum, on a water bath containing warm water to expel the dissolved ether, add 20 ml of 18 N sulfuric acid, and evaporate the solution until fumes of sulfuric anhydride are evolved.   Dilute the cooled solution to about 100 ml and nearly neutralize with ammonia.   Add 1–2 g of ammonium bisulfite and heat the solution on the hot plate for half an hour.   Now add 10–15 g of ammonium acetate, with 5–10 ml of glacial acetic acid, and boil the solution for 15 minutes.   Filter, wash with 7 per cent acetic acid, ignite, and weigh as TiO_2.

FIG. 38.

Determination of Titanium in Steel[2]

Treat 2 to 5 g of sample with 100 ml of 6 N HCl and heat until action ceases.   Dilute to 300 ml, add NH_4OH to a basic reaction, then neutral-

[1] *Z. anal Chem.*, 1901, 809

[2] Method of the U. S. Steel Corporation. Cf. Lundell, Hoffman, and Bright, *Chemical Analysis of Iron and Steel.*

ize with 6 N HCl and add 6 ml in excess. Add 10 ml of 50 per cent $Na_2S_2O_3 \cdot 5H_2O$ solution and boil 10 minutes.

If the steel contains tungsten, or a considerable residue remains after the treatment with HCl, add 100 ml of 3 per cent $NaClO_3$ solution and boil until any tungsten present is converted into yellow tungstic acid. Filter through ashless paper, and wash the residue with N HCl; reserve the filtrate. Rinse the residue on the ashless filter paper back into the original beaker, but save the filter. Digest this residue with 5 ml of 15 N NH_4OH to dissolve any WO_3, filter through the original filter, wash with N NH_4OH, and discard this filtrate. Ignite the precipitate and filter in a porcelain crucible, and add the ash to the original solution in HCl. Dilute to 300 ml, add NH_4OH until the solution is slightly ammoniacal, neutralize with 6 N HCl, and add 6 ml in excess. Add 50 ml of 50 per cent $Na_2S_2O_3 \cdot 5H_2O$ solution and boil 10 minutes. This serves to precipitate most of the titanium and reduces the iron to the ferrous state so that it does not, for the most part, precipitate.

After the treatment with sodium thiosulfate, add 3 ml of phenylhydrazine, $C_6H_5NH \cdot NH_2$, and boil 5 minutes. Phenylhydrazine is an oily liquid and is added to make the precipitation of the titanium complete. Under these conditions, it causes complete precipitation of Al, Ti, Zr, Tb, and Cr together with P and V as phosphate and vanadate, if any considerable quantity of these other five elements is present. Small quantities of Be, Ce, Cd, Fe, Hg, Ni, and Zn may be present in the precipitate.

Stir into the liquid a little paper pulp made by shaking small pieces of ashless filter paper with water in a stoppered flask; filter-paper tablets can be purchased for this purpose. Boil the mixture for 5 minutes, filter, and wash the precipitate with six 15-ml portions of hot water. Ignite carefully in a platinum crucible. Fuse the ash with a mixture of 3 g Na_2CO_3 and a little $NaNO_2$ (not KNO_3). When the melt is clear, cool, take up in 50 ml of hot water, and heat until the disintegration of the melt is complete. Filter, wash the residue containing the titanium with hot water, and discard the filtrate.

Digest the residue with hot 6 N HCl, filter, and wash with hot water. Reserve both filter and solution.

To the solution add ammonia until slightly basic and then HCl until slightly acid. Stir into the solution 1 g of $Na_2S_2O_3 \cdot 5H_2O$. Heat until the solution gives no test for Fe^{+++} when a drop is removed and tested with KCNS solution. Add 5 ml of concentrated ammonia solution in which 1 g of KCN has been dissolved, boil for 1 minute, add the reserved filter, macerate it thoroughly, and filter. Wash with hot water to which a few drops of ammonia have been added. Ignite the precipitate and filter in a crucible, and weigh. The precipitate contains TiO_2 and possibly some ZrO_2, Ta_2O_5, and SiO_2. If Zr and Ta are known to be absent a correction for SiO_2 can be made in the usual way by heating in a

platinum crucible with HF and a little H_2SO_4. Otberwise, fuse the residue with $K_2S_2O_7$ and determine tbe titanium colorimetrically (cf. p. 159). The Zr can be determined after the colorimetric determination by adding to the solution 0.5 g of $(NH_4)_2HPO_4$, keeping the solution for at least 10 hours at 50–60°, filtering, washing with 5 per cent NH_4NO_3, and weighing as $Zr_2P_2O_7$ after ignition in a crucible.

Routine Method for Titanium in Steel

Digest 1 g of sample with 40 ml of 9 N H_2SO_4. Heat until all action ceases, filter, and wash with water.

If W, Cr, or V is present, ignite the residue in a porcelain crucible at a low temperature until all carbon from the filter is consumed. Transfer to a platinum crucible and fuse with Na_2CO_3 and a pinch of $NaNO_3$. Digest the melt with hot water, filter, wash, and reject the residue. Dissolve in 6 N HCl and add to the main solution.

Dilute to 250 ml; add ammonia until a slight precipitate forms and then 5 g of $Na_2S_2O_3 \cdot 5H_2O$. If a precipitate of $Fe(OH)_3$ persists, dissolve it by adding a little H_2SO_4. Heat until the Fe^{+++} is all reduced as shown by testing a drop with KCNS solution; there should be no red color. Then add a solution of 25 ml water, 15 ml concentrated NH_4OH, and 10 g KCN. Boil 1 minute, add ashless-filter-paper pulp, filter, and wash with hot water. Ignite in a platinum crucible, fuse with 3 g of $K_2S_2O_7$, cool, dissolve the melt in 10 ml of 18 N H_2SO_4, and determine tbe titanium colorimetrically (p. 159).

Separation of Zirconium from Iron, Aluminum, Chromium, Titanium, Cerium, and Thorium

Zirconium, although almost always present in small quantities in rocks, is an element seldom determined in the past by the analytical chemist. It is very similar to titanium in its properties but is much less common. Rocks rarely contain more than 0 2 per cent of this element and usually less than 0 005 per cent. Zirconium, like titanium, although to less extent, is used in steel-making, so that the steel-works chemists are now interested in the determination of zirconium in ores and in the metals and alloys derived from them

At present the most popular method for determining zirconium[1] consists in precipitating zirconium dihydrogen phosphate, $ZrH_2(PO_4)_2$, from a cold or tepid solution containing 20 per cent by weight of concentrated sulfuric acid, by means of a large excess of diammonium phosphate In the presence of hydrogen peroxide, titanium is not precipitated In this way zirconium can be precipitated in the presence of iron, aluminum, chromium, cerium, and thorium.

[1] Bailey, *J. Chem. Soc.*, 49, 149, 481 (1886); Steiger, *J. Wash. Acad. Sci.*, 8, 637 (1918); Nicolardot and Reglade, *Compt rend*, 168, 348 (1919); Johnson, *Chem. Met Eng.*, 20, 588 (1919); Ferguson, *Eng. Mining J*, 106, 793 (1918); Hillebrand, *Analysis of Silicate and Carbonate Rocks*, p. 173, 1919; Lundell and Knowles, *J. Am. Chem. Soc*, 41, 1801 (1919), and *J. Ind. Eng. Chem.*, 12, 562 (1920).

Procedure. For small quantities of zirconium (0.5 mg) the volume of the solution should be reduced to 25 ml before attempting to precipitate zirconium phosphate. With larger quantities, the volume should be increased and amount to 200 ml for the precipitation of 0.1 g of zirconium. To the neutral solution add concentrated sulfuric acid until 20 per cent by weight is present. Add sufficient hydrogen peroxide to change all the titanium to pertitanic acid and at least 10 times as much ammonium phosphate as required theoretically to form $ZrH_2(PO_4)_2$. For small quantities of zirconium an excess of 100 times the theoretical quantity is desirable. Keep the solution at 40–50° for 2 hours if more than 5 mg of zirconium is present, and for at least 6 hours if the quantity of zirconium is smaller. Decant as much as possible of the supernatant liquid through a filter and wash with cold 5 per cent ammonium nitrate until the excess ammonium phosphate is removed. Do not wash with pure water as it causes hydrolysis of the precipitate, leaving less phosphoric acid in proportion to the zirconium. Moreover, it is easier to get a white, ignited precipitate when the filter and precipitate contain some ammonium nitrate. Ignite very carefully in an open crucible using a low flame until all the filter-paper carbon has been consumed; then raise the temperature to the full heat of a Méker burner or the blast lamp. Weigh as ZrP_2O_7.

If the weight of the precipitate exceeds a few centigrams, it is better to fuse with sodium carbonate, extract the product with hot water, and weigh the residue as ZrO_2.

Determination of Zirconium, Aluminum, and Titanium in Steel

Dissolve 5 g of steel in 50 ml of 12 N HCl and add small portions of concentrated HNO_3 until all the iron is oxidized to the ferric state. Evaporate to dryness, moisten the residue with 10 ml of 12 N HCl, and repeat the evaporation, this time baking somewhat to remove any nitrates that may remain. Take up the residue in 50 ml of 6 N HCl and heat until all the ferric oxide and basic salts are dissolved. Filter, wash the impure silica residue with hot 3 per cent hydrochloric acid, and save the filtrate.

Ignite the impure silica and determine its weight if it is desired to know the silicon content of the steel. Treat with HF and H_2SO_4 as described under "Silicic Acid." Fuse the slight residue with a little $K_2S_2O_7$ (see p. 174). Dissolve the melt in 15 ml of N H_2SO_4 and add the solution to the acid extract obtained after the ether separation described in the second paragraph on p. 183.

If the steel contains tungsten fuse the residue, after the treatment with HF, with 6 g Na_2CO_3, cool, and digest the melt with hot water. Add ashless-filter-paper pulp, filter, and wash with 2 per cent NH_4NO_3 solution. Discard the filtrate but add the filter and residue to the original platinum crucible, ignite, fuse with $K_2S_2O_7$, extract the melt with dilute sulfuric acid, and add to the acid extract obtained after treatment with ether as described in the next paragraph.

Evaporate the filtrate and washings from the silica determination to sirupy consistency, add 40 ml of 6 N hydrochloric acid, and extract with ether as described on p. 179. The ether extract will contain most of the iron and molybdenum, and the acid extract will contain some iron and all the zirconium, titanium, aluminum, manganese, chromium and copper, etc., that was present in the steel. Discard the ether extract.

Evaporate the ether from the acid extract, add the sulfuric acid solution obtained after the removal of the silica, and heat with 0.5 ml of concentrated nitric acid to make sure that all the residual iron is in the ferric condition. Dilute to 200 ml, and precipitate the iron, zirconium, titanium, manganese, nickel, etc., by adding 20 per cent sodium hydroxide, with 10 ml in excess. The caustic alkali used should be pure and free from carbonate. Dissolve the precipitate in hot 6 N hydrochloric acid, and repeat the treatment with caustic soda solution. Use the combined filtrates for the aluminum determination and this last precipitato for the determination of zirconium and titanium.

Dissolve the precipitate in hot 6 N hydrochloric acid. Inasmuch as zirconium phosphate is not easily dissolved by acid, it is possible for some zirconium to be left on the filters used for retaining the sodium hydroxide precipitate. To recover this, ignite the filters in a platinum crucible, fuse the ash with sodium carbonate, and extract the sodium salts in the melt by treatment with hot water. Discard this aqueous solution, dissolve the residue in hot 6 N hydrochloric acid, and add the solution to that containing the greater part of the zirconium.

Determination of Aluminum. In the absence of chromium, uranium, and vanadium, add a few drops of methyl red indicator solution, neutralize with hydrochloric acid, and add 4 ml of concentrated acid in excess for each 100 ml of solution. Make barely alkaline with ammonia, boil 3 minutes, and set aside for 10 minutes. If no precipitate forms, the absence of aluminum is assured. If a precipitate is obtained, filter it off and discard the filtrate. Without washing the precipitate, dissolve it in as little hot 6 N hydrochloric acid as possible. Dilute to 50 ml, neutralize with ammonia, and add 2 ml of concentrated nitric acid. Heat to 50° and precipitate phosphorus with ammonium molybdate as described under the "Determination of Phosphorus in Steel

by the Blair method." Filter and wash with ammonium acid sulfate solution and discard the precipitate of ammonium phosphomolybdate. Precipitate the aluminum hydroxide again with ammonium hydroxide as described above. Filter, discard the filtrate, redissolve in hot 3 N hydrochloric acid, and reprecipitate. After washing with 2 per cent ammonium nitrate, ignite and weigh as Al_2O_3. After so much manipulation, this precipitate is certain to contain a little silica from the reagents and glassware. It should be treated with sulfuric and hydrofluoric acid to volatilize silicon fluoride as described under "Silicic Acid," or a blank may be made carrying out every operation described above with a solution containing no iron or aluminum.

If the steel contains chromium, proceed as above until the filtrate from the ammonium phosphomolybdate precipitate is obtained. Continue as above, but before the first precipitation of the aluminum hydroxide and phosphate, add a little sodium peroxide to oxidize the chromite to chromate. Then use nitric acid instead of hydrochloric acid to neutralize the alkaline solution. The first precipitate produced by ammonia will then be free from chromium.

If the steel contains uranium, use ammonium carbonate instead of ammonium hydroxide for the final precipitation of the aluminum.

If the steel contains vanadium, the weighed Al_2O_3 will contain some vanadium. Fuse the precipitate with potassium pyrosulfate, extract the cold melt with 5 per cent sulfuric acid, and determine the vanadium content as described under "Vanadium." Make a corresponding deduction from the weight of impure alumina.

Determination of Zirconium and Titanium. Dilute the hydrochloric acid solution, obtained after dissolving the sodium hydroxide precipitate in the preceding directions, to 250 ml. Neutralize partly with ammonium hydroxide but leave about 5 per cent by volume of 6 N hydrochloric acid. Add 2 g of tartaric acid and precipitate any copper by introducing hydrogen sulfide. Filter if necessary. Add ammonia to the solution which is saturated with hydrogen sulfide and introduce more of the gas. Filter and wash with water containing 2 per cent of ammonium chloride and a little ammonium sulfide. If a precipitate forms in the filtrate, heat to boiling and filter through a new filter. The precipitate contains, besides FeS, most of the manganese and all the nickel and cobalt as sulfides. It is advisable to determine these elements in another portion of the steel.

Neutralize the ammonium sulfide filtrate with sulfuric acid, and add 30 ml of concentrated acid in excess. Digest on the steam bath until sulfur and sulfides have coagulated. Filter; wash with 100 ml of 10 per cent sulfuric acid by volume. Cool the filtrate in ice water.

Slowly add, with stirring, an excess of a cold 6 per cent solution of cupferron (ammonium nitrosophenylhydroxylamine). The excess of the reagent is shown by the formation of a white cloud on adding the reagent and the cloud disappears instead of forming a permanent coagulated precipitate. After waiting 10 minutes, filter with gentle suction and wash thoroughly with 10 per cent hydrochloric acid. Discard the filtrate. Carefully ignite in a weighed platinum crucible and weigh the ZrO_2 and TiO_2.

Fuse the weighed oxides with potassium pyrosulfate and determine the titanium colorimetrically as described on p. 159. Deduct the corresponding weight of TiO_2 from the weight of the two oxides, or carry out the tannin separation described on p. 223.

Remarks. Phosphorus does not interfere appreciably. Vanadium causes some trouble. If present in the steel, fuse the weighed cupferron precipitate with sodium carbonate and determine the vanadium in the water-soluble extract. Fuse the insoluble residue with potassium pyrosulfate and determine the titanium colorimetrically.

Uranium may interfere slightly when present in the quadrivalent state. If this element is suspected, boil off all the hydrogen sulfide before the cupferron precipitation and oxidize the uranium to the sexivalent condition by means of permanganate and then proceed with the cupferron precipitation.

Thorium and cerium interfere but are not thrown down quantitatively with the zirconium and titanium. If these elements are suspected, proceed as follows: Take the solution after the colorimetric determination of titanium and add an excess of potassium hydroxide solution. Filter and wash once or twice by decantation and then a few times on the filter with water. Transfer to a platinum dish, add hydrofluoric acid, and evaporate nearly to dryness. Take up in 5 ml of 5 per cent hydrofluoric acid (by volume). If no precipitate is visible, the rare earths are absent. If a precipitate is obtained, filter off the fluorides on a small filter resting in a Bakelite funnel or a glass funnel thoroughly coated with paraffin on the inside. Wash the crude fluorides back into the platinum dish, add the ash of the filter, and evaporate to dryness with a little sulfuric acid. Take up in hydrochloric acid and precipitate the rare earth hydroxides with ammonia. Filter, redissolve in hydrochloric acid, evaporate to dryness, and treat the residue with 5 ml of boiling-hot 5 per cent oxalic acid solution. After 15 minutes, filter, wash with less than 20 ml of 5 per cent oxalic acid, ignite, and weigh. Multiply the weight obtained by 1.18 to allow for an imperfect separation of the rare earths, and deduct the weight from that of the ZrO_2 obtained by the above procedure.

Separation of Beryllium (Glucinium) and Uranium

These two elements rarely occur together except in a few minerals. Neither of them is precipitated in the cold by adding an excess of ammonium carbonate to the acid solution, and in this respect they are different from iron and aluminum. By boiling the ammonium carbonate solution, however, basic beryllium carbonate is precipitated. If the boiling is continued long enough to make the precipitation of the beryllium quantitative, some uranium is thrown down, probably as ammonium

uranate, $(NH_4)_2U_2O_7$. Hydroxylamine serves to prevent the precipitation of the latter compound by ammonium hydroxide but it does not prevent precipitation of beryllium hydroxide. Brinton and Ellestad[1] found it possible to develop a satisfactory method of separating beryllium and uranium by using both ammonium carbonate and hydroxylamine hydrochloride.

Procedure. To the hydrochloric acid solution containing not more than 0.2 g beryllium and 0.3 g uranium in a volume of about 250 ml, add 5 g of ammonium chloride, unless already present, and 5 g of hydroxylamine hydrochloride. Add concentrated ammonium carbonate solution until the precipitated carbonates dissolve completely in the excess of reagent. Heat to boiling and continue boiling for 30–60 seconds after the heavy white precipitate of basic beryllium carbonate forms. Filter without delay and wash thoroughly with cold water. This precipitate will contain the greater part of the beryllium and should contain no uranium.

Add hydrochloric acid in slight excess to the filtrate and heat to remove all the carbon dioxide. Add 1 g more of hydroxylamine hydrochloride and a slight excess of ammonium hydroxide after the solution has cooled. This causes the precipitation of the remainder of the beryllium as $Be(OH)_2$. Filter and wash with 2 per cent ammonium nitrate solution containing a little hydroxylamine hydrochloride. Ignite the two precipitates in a crucible, finally heating over the blast or Méker burner, and weigh as BeO.

To determine uranium, make the filtrate from the last precipitation acid with hydrochloric acid, and to the cold solution add small portions of alkali bromate (keeping the beaker covered with a watch glass to prevent loss by spattering) until the solution shows the color of dissolved bromine. In this way the hydroxylamine is oxidized. Heat the solution to boiling and precipitate ammonium uranate from the hot solution by adding a slight excess of ammonium hydroxide. Wash with 2 per cent ammonium nitrate solution containing a little ammonia but no hydroxylamine hydrochloride. Ignite and weigh as U_3O_8.

Separation of Uranium from Iron and Aluminum

Treat the slightly acid solution, containing considerable quantities of ammonium salts, with an excess of ammonium carbonate and then with ammonium sulfide, allow to stand for some time in a closed flask, finally filter, and wash with water containing ammonium sulfide.

The precipitate contains the iron as sulfide and the aluminum as hydroxide; in the filtrate is found all the uranium as $(NH_4)_4UO_2(CO_3)_3$.

[1] *J. Am. Chem. Soc.*, 45, 395 (1923).

Dissolve the precipitate in hydrochloric acid. Expel hydrogen sulfide by gently boiling, oxidize the ferrous salt to ferric salt by the addition of nitric acid, and determine the iron and aluminum by one of the methods described on pp. 167–172.

Evaporate the filtrate containing the uranium almost to dryness, make acid with hydrochloric acid, boil, and precipitate the uranium as ammonium uranate by the addition of ammonia which contains no carbonate. Filter off the precipitate promptly, wash with 2 per cent ammonium nitrate solution to which a little ammonia has been added, dry, ignite, and weigh as U_3O_8.

The result obtained can be verified by heating the residue repeatedly in a current of hydrogen in a Rose crucible (see "Copper Determination") until a constant weight of UO_2 is obtained. The purity of the precipitate can also be tested volumetrically (see Chapter XV).

Separation of Beryllium from Aluminum

Beryllium, although a bivalent metal of Group II in the periodic classification, resembles aluminum in its reactions. Ordinarily it is determined as BeO after precipitation with NH_4OH. Because of the colloidal nature of the precipitate, the results are likely to be a little high. Moser[1] recommends the first two of the following methods of precipitating $Be(OH)_2$.

(a) To the slightly acid solution containing about 0 1 g of BeO in 100 ml, add sodium carbonate till a slight turbidity results, dissolve this in hydrochloric acid, heat to 70° and, while passing a current of air through the solution, add 50 ml of 6 per cent ammonium nitrite and 20 ml of methyl alcohol. The current of air helps to remove nitrous fumes, and the alcohol serves to form nitrous ester.

(b) Dilute the solution containing about 0 1 g of BeO to 300–400 ml, add 20–30 g of ammonium nitrate, and heat to boiling. Add about 1.25 g of tannin and ammonium hydroxide, drop by drop, until no further precipitation takes place If alkali cation is present, and no other cation is permissible, dissolve the precipitate in dilute hydrochloric acid and repeat the precipitation as before

(c) The following method for separating beryllium from aluminum depends on the fact that, by fusing a mixture of BeO and Al_2O_3 with sodium carbonate, the former oxide is unattacked and the latter is transformed into water-soluble sodium aluminate.[2]

Procedure. Fuse the oxides for 2 to 3 hours with 5 g of sodium carbonate at a temperature slightly above the melting point of the flux. Cool, digest the melt with 300 ml of water on the steam bath, filter, and wash the undissolved residue thoroughly with hot water. Ignite strongly and weigh as BeO. In the filtrate determine the aluminum by Blum's method (p. 148).

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[1] Moser and Singer, *Monatsh*, **48**, 673 (1927).
[2] Wunder and Wenger, *Z. anal. Chem*, **51**, 470 (1912).

If the original oxides weighed only about 0.25 g, a single fusion usually suffices to accomplish a satisfactory separation; but if more is used it is advisable to fuse again with sodium carbonate and repeat the above treatment.

Hillebrand and Lundell[1] state that the best methods for separating beryllium from aluminum are those in which the aluminum is precipitated by 8-hydroxyquinoline (p. 151) or as chloride by passing HCl gas into a cold solution of the two chlorides in a mixture of equal parts concentrated HCl and ether. Parsons and Barnes[2] recommended precipitating the aluminum in a boiling 10 per cent solution of NaHCO₃, but some beryllium is always carried down with the alumina and the separation is unsatisfactory in the presence of phosphate which causes precipitation of Be, Ti, Zr., etc.

(b) DIVISION OF THE PROTOXIDES

MANGANESE, NICKEL, COBALT, ZINC

MANGANESE, Mn.   At. Wt. 54.93

Forms: $MnSO_4$, MnS, Mn_3O_4, $Mn_2P_2O_7$

1. Determination as Manganous Sulfate, $MnSO_4$

This method, first proposed by Volhard,[3] gives accurate results provided that no other sulfate is present. Heating at 450–500° for an hour[4] is sufficient to remove all moisture and excess sulfuric acid. Long heating (17 hours) at 580° causes slight darkening, but even then the results are accurate.

Dissolve the oxide obtained by the ignition of the carbonate, sulfide, or of manganous manganite, in as little as possible of strong sulfuric acid, and some sulfurous acid if necessary to reduce Mn_3O_4, in a porcelain crucible. Evaporate as far as possible on the water bath, remove the excess acid by heating in an electric oven, gradually raise the temperature to 450°, and keep it there for 30 minutes. The heating can take place in an air bath (p. 31). When the air bath is used, finally cover both crucibles and heat over a good Bunsen burner for 10 minutes.

(a) Precipitation of Manganese as Carbonate

This method is suitable only for the determination of manganese in solutions of pure manganese salts containing nothing else except alkali and ammonium salts.

[1] *Applied Inorganic Analysis.*

[2] *J. Am. Chem. Soc*, 28, 1589 (1906).

[3] *Ann. Chem. Pharm.*, 198, 328 (1879). Cf. Marignac, *Arch. sci. phys. nat.* [3], 10, 25 (1883); Meineke, *Chem. Ztg.*, 9, 1478, 1787 (1885); Friedheim, *Z. anal. Chem.*, 38, 637 (1899); Gooch and Austin, *Am. J. Sci.*, 5, 209; Blum, *J. Am. Chem. Soc.*, 34, 1382 (1912).

[4] Blum recommends a longer period of heating, but in his experiments he was working with 2.4 g of manganous sulfate and considered the weight constant only when the variation was less than 0.3 mg after heating for protracted periods.

According to H. Tamm,[1] the precipitation is best accomplished by means of ammonium carbonate. For this purpose treat the neutral solution (which may contain other ammonium salts) with a slight excess of ammonium carbonate, heat gently, and allow the beaker containing the solution to remain in a lukewarm water bath until the precipitate has settled and the upper liquid has become clear.

Filter off the precipitate, wash with hot water, dry, ignite, and weigh as sulfate as described above.

Remark. If either sodium or potassium carbonate is used to precipitate the manganese, the precipitate will always contain alkali carbonate that cannot be removed by washing. After the precipitate has been ignited, however, the alkali carbonate can be easily extracted by water Furthermore, the precipitation is not quite quantitative; the filtrate always contains small amounts of manganese.

(h) Precipitation of Manganese as Sulfide

This method is employed when it is necessary to separate manganese from calcium, strontium, barium, and magnesium. To the acid solution, which contains not more than 0.3 g of manganese and no other cation that forms an insoluble sulfide, together with enough ammonium salt to prevent precipitation of magnesium as hydroxide, add concentrated NH_4OH and 2 ml in excess. Transfer the solution to a 250-ml Erlenmeyer flask and dilute to about 150 ml. Saturate with H_2S, add 2 ml more of NH_4OH, and dilute with recently boiled and cooled water to the neck of the flask. Stopper the flask and allow to stand over night. Filter uninterruptedly through paper, and wash with a cold 2 per cent solution of NH_4Cl containing a little NH_3 and H_2S. Keep the funnel nearly filled with liquid all the time, to prevent atmospheric oxidation. Dissolve the washed precipitate of manganous sulfide in dilute hydrochloric acid, evaporate the solution to dryness to remove all hydrogen sulfide, dissolve the residue in a little water, transfer the solution to a weighed crucible, and determine as sulfate. Manganous sulfide can also be weighed as such. (See p. 190.)

(c) Separation of Manganese as Manganese Dioxide

If a dilute solution of a manganous salt is treated with bromine water and boiled, the reaction

$$MnCl_2 + Br_2 + 2H_2O \rightleftarrows MnO_2 + 2HCl + 2HBr$$
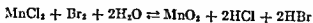
does not take place unless the halogen acids are neutralized as fast as they are formed. This neutralization can be accomplished by means of the salt of a weak acid, such as sodium acetate, even when the solution contains free acetic acid, which is very slightly

[1] *Chem. News*, 26, 37 (1872), and *Z. anal. Chem.*, 11, 425 (1872).

ionized in the presence of its alkali salt. Thus in a solution such as is obtained after the removal of iron and aluminum by a basic acetate separation (cf. p. 209), the manganese can be precipitated quantitatively by boiling with an excess of bromine water. The oxide does not correspond exactly to MnO_2, although most of the manganese is in the quadrivalent condition.[1] When the precipitate has collected in large flocks, discontinue the boiling and allow the precipitate to settle; filter, and wash with hot water. Some chemists ignite this precipitate and weigh as Mn_3O_4, but it is more accurate to dissolve the precipitate in a mixture of HCl and H_2SO_4 and to precipitate the manganese finally as manganese ammonium phosphate. (See 4, p. 191.)

Chlorine, hydrogen peroxide, hypochlorites, etc., may be used instead of bromine but these reagents have no special advantages.

If the solution of the manganous salt also contains ammonium salts the precipitation of the manganese does not take place by the above procedure, because the sodium acetate serves rather to neutralize the acid set free by the following reaction:

$$2NH_4Cl + 3Br_2 = N_2 + 2HCl + 6HBr$$
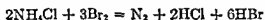
Upon the addition of ammonia, however, the precipitation of the manganese can be effected. In this case, it seems fair to assume that the reaction goes through the following stages:

$$MnCl_2 + 2NH_4OH \rightleftharpoons Mn(OH)_2 + 2NH_4Cl$$

$$Mn(OH)_2 + Br_2 + 2NH_4OH = MnO(OH)_2 + 2NH_4Br + H_2O$$
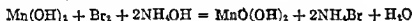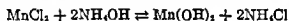
The precipitation with bromine and ammonia is not so satisfactory as with bromine alone because when ammonia or ammonium salt is present much of the bromine is used up in oxidizing them. In that case there is considerable evolution of nitrogen, and, moreover, when an excess of bromine is added the solution may become acid enough to dissolve the precipitated manganese.

$$2NH_3 + 3Br_2 = 6HBr + N_2$$

It is necessary, therefore, when ammonium salts are present to make sure that the solution is ammoniacal at the end of the operation.

This method of precipitating manganese from solutions possesses disadvantages which make it useless in many cases. If, besides manganese, the solution contains calcium, zinc, etc., manganites of these metals are precipitated with the manganese. In this case the precipitate must be dissolved in hydrochloric acid and the precipitation repeated several times, but even then it is not possible to obtain a precipitate altogether free from these metals. If the other metals are present only in small amounts, the results obtained by this method are sufficiently accurate. The precipitation of manganese as sulfide in the presence of other metals is always satisfactory and should be used almost invariably.

2. Determination of Manganese as Sulfide

If the manganese has been precipitated, as described on p. 189, as sulfide, separate the precipitate from the filter as completely as possible,

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[1] The MnO_2 acts as the anhydride of metamanganous acid, H_2MnO_3, and some manganous manganite, $MnMnO_3$ or Mn_2O_3, is contained in the precipitate.

place in a Rose crucible (of unglazed porcelain) (Fig. 23, p. 67), burn the filter in a platinum spiral, and add the ash to the main portion of the precipitate. Add some pure sulfur which has been crystallized from CS_2, and heat the crucible and its contents in a current of hydrogen. After the excess of sulfur has distilled off and burned, cool the crucible in the stream of hydrogen and weigh the precipitate as MnS.

3. Determination of Manganese as Mn_3O_4

Inasmuch as all the oxides of manganese, as well as those compounds which are converted into oxide on ignition (manganous salts of volatile organic and inorganic acids, with the exception of the halogen salts), are converted into Mn_3O_4[1] on being heated in the air, at temperatures between 940° and 1100°, it follows that this method for the determination of manganese is quite generally applicable. It is nearly as accurate as the methods described under 1 and 2, if the ignition of the precipitate takes place in an electric furnace at about 1000°, and very good results are obtained if, as recommended by Gooch,[2] the porcelain crucible (containing the carbonate, manganous manganite, or sulfide) is entirely surrounded by the oxidation flame of a Teclu burner, whereby a moderately high heat is obtained without too much free access of air.

After the ignition, cool the crucible and its contents in a desiccator and weigh the Mn_3O_4.

4. Determination of Manganese as Pyrophosphate, $Mn_2P_2O_7$

This excellent method was recommended by W. Gibbs[3] and subsequently studied by Gooch and Austin;[4] it is probably the best gravimetric method for determining manganese.

To the slightly acid solution, containing manganese equivalent to not more than 0.5 g $Mn_2P_2O_7$ in 250 ml, and no other metals except alkalies, add 20 g of NH_4Cl and 1 to 2 g of diammonium phosphate $(NH_4)_2HPO_4$. Heat to boiling, clear the solution if necessary with a few drops of 6 N HCl, and then add dilute NH_4OH dropwise with constant stirring. As soon as a precipitate appears stop adding NH_4OH and stir until the precipitate assumes a silky, crystalline appearance. Continue boiling all the time. Finally add 0.5 ml of concentrated NH_4OH and cool,

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[1] Cf. R. J. Meyer and K. Retgers, *Z. anorg. Chem*, 57, 104 (1908), at 530° the oxides of manganese are slowly but quantitatively changed into Mn_3O_4.

[2] *Z. anorg. Chem.*, 17, 268 (1898).

[3] *Am. J. Sci.*, 46, 216; *Z. anal. Chem.*, 7, 101 (1868).

[4] *Z. anorg. Chem.*, 18, 339 (1898).

preferably in ice water. Let stand 2 to 3 hours, filter through paper or into a Gooch crucible, wash with cold, slightly ammoniacal, 10 per cent ammonium nitrate solution, dry, and heat to constant weight at about 1000°. If a paper filter is used heat at as low a temperature as possible until all carbon is removed. Cool in a desiccator and weigh as $Mn_2P_2O_7$.

Manganese can be determined very accurately by volumetric methods (see Chapter XV).

5. Colorimetric Determination of Manganese

Small quantities of manganese can be determined accurately and quickly by a *colorimetric method*. The method depends upon the oxidation of Mn^{++} to strongly colored MnO_4^- and can be accomplished by such agents as alkali periodate, ammonium persulfate in the presence of silver ions, sodium bismuthate, or lead dioxide. Alkali periodate or ammonium persulfate in the presence of silver ions is usually preferred because no filtration is necessary. The reactions are:

$$2Mn^{++} + 5S_2O_8^{--} + 8H_2O + [Ag^+] \rightarrow 2MnO_4^- + 10SO_4^{--} + 16H^+ + [Ag^+]$$

$$2Mn^{++} + 5IO_4^- + 3H_2O \rightarrow 2MnO_4^- + 5IO_3^- + 6H^+$$
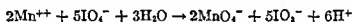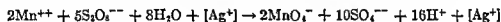
Procedure. Free the solution from reducing agents, if necessary, by boiling with nitric acid. If an insoluble carboniferous residue is present, as in the analysis of cast iron, it should be filtered off. Carbides, which are present in solution when steel is analyzed, should be oxidized by boiling with a little $(NH_4)_2S_2O_8$. If chlorides are present, evaporate with nitric and sulfuric acids until fumes of the latter appear. When ready for the test, 100 ml of the solution should contain the equivalent of 20 ml concentrated nitric acid and in addition 10–15 ml of concentrated H_2SO_4 or 5–10 ml of sirupy H_3PO_4 or a mixture of H_2SO_4 and H_3PO_4. The colorimetric comparison is best made with not over 1 mg of Mn in 50 ml of solution.

With Periodate. Add 0.2–0.4 g of KIO_4 or $NaIO_4$ or 0.3–0.5 g of $Na_2H_2IO_6$. Boil 1 minute, keep hot 5–10 minutes, dilute to the proper volume, and compare with standards of known manganese content which have been treated in the same way.

With Persulfate. Add 15 ml of 0.1 N $AgNO_3$ solution and 1 g of $(NH_4)_2S_2O_8$. Heat to develop the color, and continue heating for 30 seconds after the oxidation starts and bubbles of oxygen appear from decomposition of the persulfate. Cool and compare with standards which have been treated in the same way. A colorimeter is convenient but Nessler tubes are satisfactory.

NICKEL, Ni. At. Wt. 58.69

Forms: Nickel Dimethylglyoxime, $NiC_8H_{14}N_4O_4$; Nickel, Ni; and Nickel Oxide, NiO

1. Determination as Nickel Glyoxime

Dimethylglyoxime, CH_3 CNOH·CNOH·CH_3, was recommended by L. Tschugaeff[1] as a reagent for nickel and used by K. Kraut[2] for detecting the presence of traces of nickel in ashes. O. Brunck[3] and others have also studied the reaction and have found it to furnish a most rapid and accurate method for the exact estimation of nickel either by itself or in the presence of cobalt, zinc, and manganese. If the solution contains tartaric acid enough to prevent the precipitation of iron by ammonia, the nickel in a sample of nickel steel can be determined accurately within 2 hours and without the removal of any other metal.

When a dilute, neutral solution of a nickel salt is treated with an alcoholic solution of dimethylglyoxime, a red, crystalline precipitate of nickel dimethylglyoxime is formed.

$$NiCl_2 + 2(CH_3)_2C_2(NOH)_2 = [(CH_3)_2C_2NOH\ NO]_2Ni + 2HCl$$
$$\underset{\text{Dimethylglyoxime}}{} \qquad \underset{\text{Nickel dimethylglyoxime}}{}$$
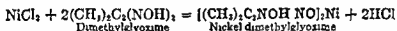
The salt is soluble in mineral acids so that precipitation is incomplete because of the acid set free in the reaction. It becomes quantitative, however, if the mineral acid is neutralized by ammonia or if sodium acetate is added, whereby the mineral acid is replaced by acetic acid in which the precipitate is practically insoluble. Large quantities of ammonium salts or of alkali acetate do no harm, but no excess of ammonia tends to retard the formation of the precipitate. The precipitate is distinctly soluble in absolute alcohol, but only traces dissolve in 50 per cent alcohol, and in more dilute alcohol it is even less soluble. When thrown down in the cold or in the presence of much free ammonia the precipitate is very voluminous and hard to filter.

Ferrous iron gives a deep red compound with dimethylglyoxime and ammonia; traces of ferrous iron can be detected in this way. The presence of a little ferrous iron does not, however, hurt the results and good values are obtained even when the color becomes deep red on standing after the addition of the reagent. If the solution is allowed to stand for some time before the nickel precipitate is filtered off, and an excess of reagent was used, some dimethylglyoxime often precipitates and can be seen in the form of long, white needles on top of the red nickel precipitate in the filtering crucible. This can be removed by washing with 50 per cent ethyl alcohol. The method is very accurate and can serve for determining large as well as small quantities of nickel, provided that not more than 0.1 g of Ni is present in the solution analyzed.

Procedure. Dilute the neutral or slightly acid[4] solution so that not more than 0.05 g of nickel is present in 200 ml, heat nearly to boiling, and treat with a slight excess of a 1 per cent solution of dimethylglyoxime

[1] Z anorg. Chem, 46, 144 (1905). Ber, 38, 2520 (1905).

[2] Z angew Chem, 19, 1793 (1906); ibid, 20, 1844 (1907).

[3] Ibid, 20, 834 (1907); Stahl u Eisen, 23, 331.

[4] If strongly acid, neutralize with NH_4OH.

in ethyl alcohol.[2] Carefully add ammonia until the solution smells slightly of it after blowing away the fumes. Allow to stand an hour if convenient, filter, while still hot, into a Gooch or Munroe crucible, wash with hot water, and dry at 110° to 120° for 45 minutes. The precipitate contains 20.31 per cent Ni.

The nickel salt of dimethylglyoxime is red and crystalline. It contains no water of crystallization and sublimes at 250° without decomposition. Examine the precipitate in the crucible to see if any white needles of dimethylglyoxime are present. If found, dissolve them by washing with 50 per cent ethyl alcohol.

2. Determination of Nickel as Metal by Electrolysis

Nickel is above hydrogen in the potential series of the elements so that from acid solutions it is easier to discharge hydrogen ions than to deposit nickel, unless a mercury cathode is used. W. Gibbs[3] showed, however, that it is easy to get complete deposition upon the cathode when the nickel solution is strongly ammoniacal and contains considerable ammonium salt. A suitable electrolyte can be obtained by adding excess ammonia and ammonium salt to a solution containing nickel as sulfate or chloride. The presence of nitrate is usually avoided although it has been found possible to effect complete deposition of nickel from a nitrate solution provided that no nitrous acid is present. Nitrous acid can be removed from a solution of a metal
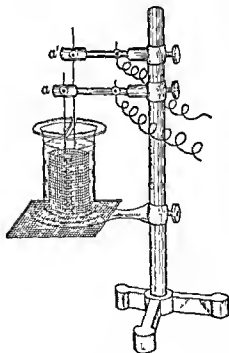
in nitric acid by gentle boiling or by treating the solution with urea, $CO(NH_2)_2$. In the electrolysis of nitrate solution an anode of passive iron has been recommended. This can be obtained by taking an iron wire of 1.5-mm diameter, cleaning it in HCl, dipping it into 15 N HNO_3, and promptly washing it with water and alcohol. When a platinum anode is used with a nitrate solution, a little platinum goes into solution at the anode and is deposited on the cathode; this causes high results in the nickel determination.

A suitable electrolytic cell consists of a 125-ml beaker, a platinum gauze cathode, and a smaller gauze or spiral anode (Fig. 39). The cathode should reach to the bottom of the beaker, and the top of the gauze cylinder should extend a little above the surface of the liquid. It may be desirable to use a platinum dish as cathode, as recommended by Classen.

The electrodes can be connected with an electrode stand on which metal arms are attached to an upright glass rod (Fig. 39).

Fig. 39.

[1] Use 40 ml of 1 per cent solution for 0.1 g of nickel.
[2] Z. anal. Chem., 3, 334 (1864); cf. Fresenius and Bergmann, ibid., 19, 320 (1880).

To prevent serious loss of electrolyte by spattering, cover the beaker with two halves of a watch glass This is not entirely satisfactory, as when much gas is evolved a little of the liquid is still carried off mechanically. This method of fastening the electrodes, moreover, has the disadvantage that, when the electrolysis is carried out in a hot solution, acid or ammoniacal vapors, as the case may be, condense on the brass arms of the electrode support; some of the liquids thus condensed dissolve brass, and the resulting solution may drop into the beaker and spoil the analysis To prevent this, it is better to bend the ends of the electrodes to a right angle and connect with an electrode stand designed as shown in Fig. 40.
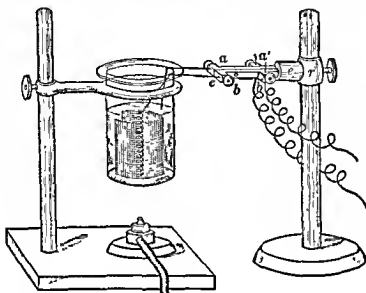
FIG. 40.

This electrode holder consists of two brass rods insulated from each other by means of an intervening layer of mica, and the rods are fastened to the ring r through a piece of ebonite, e The openings to hold the wires are cut wedge-shaped, so that wire of any shape can be inserted.

Since the ends of the electrodes leave the beaker in a horizontal direction, the beaker can be covered tightly by means of a whole watch glass, and not only are losses by spattering avoided, but there is absolutely no danger of contamination from the outside.

Originally all electrolytic determinations were made with stationary electrodes and a weak current was passed through the solution for a long time. If too strong a current was used, very often the deposits were spongy and did not adhere well to the electrodes This was due to the fact that hydrogen gas began to form at the cathode before the deposition of the metal was anywhere nearly complete. It was found, however, that by stirring the electrolyte or by heating it so that the ions of the metal were kept constantly in contact with the cathode without waiting for their transference through the solution as a result of electric attraction, the current could be increased considerably and the time required shortened correspondingly. Thus by working in a concentrated solution and with a stirred electrolyte it is possible to deposit all the copper from a solution in a few minutes, whereas formerly about 20 hours would have been recommended. The Braun electrolytic apparatus (Fig. 21 on p. 74) has been found very satisfactory for such work with stirred electrolytes.

The Electrolysis of Ammoniacal Nickel Solution

For every 0.25–0.30 g nickel present as sulfate or chloride but not as nitrate,[1] add 5–10 g of ammonium sulfate and 30–40 ml of concentrated ammonia; dilute the solution with distilled water to a volume of 150 ml. Electrolyze this solution at the room temperature with a current of 0.5–1.5 amperes and a potential difference between the electrodes of 2.8–3.3 volts. The electrolysis is finished in about 2 hours, as can be shown by adding a little water and allowing the current to pass through the solution for 15 or 20 minutes longer. If at the end of this time no nickel has deposited upon the electrode surface which was wet for the first time by the last dilution, the determination is finished. If the solution is kept at a temperature of 50–60° C, only about 1 hour is necessary for the deposition, and the deposit adheres better to the electrode and is bright, possessing almost the color of platinum.

As soon as the electrolysis is finished, remove the watch glass, raise the electrode holder so that only the bottoms of the electrodes remain in the liquid, and wash the upper parts of the electrodes thoroughly with water from a wash bottle. Then raise the electrodes entirely out of the solution and wash the bottoms immediately with water. Turn off the current, rinse the cathode with alcohol, dry by heating at 105° for a few minutes, cool, and weigh.

To clean the cathode, place it in a small beaker, add enough 6 N nitric acid to wet all the nickel, and heat for at least 15 minutes. This treatment is absolutely necessary to remove the last traces of nickel. If this is not done, the electrode on being ignited becomes discolored, and it is then very difficult to clean the electrode by repeated treatment with acid followed by ignition. The addition of a little copper salt to the nitric acid helps to dissolve the nickel deposit. To make sure that all the nickel has been deposited from the electrolyzed solution, nearly neutralize the ammonia with hydrochloric acid and add a few cubic centimeters of a 1 per cent solution of dimethylglyoxime in alcohol. When less than 0.1 mg of nickel is present, it will take several minutes for a yellow coloration to appear, and soon afterward the red crystals of nickel salt will be precipitated.

The nickel not deposited by an electrolysis may be estimated accurately by shaking the solution thoroughly and comparing the color produced by the addition of dimethylglyoxime with that produced with a dilute nickel solution containing a known quantity of nickel. Naturally such a colorimetric test can be used only with very small quantities of nickel.

Remark. The electrolysis of nickel from an ammoniacal solution should not be continued for too long a time, because the cathode slowly gains in weight even after all the nickel has been deposited from the solution. The anode is attacked, causing platinum to go into solution, which is deposited upon the cathode, partially, at least.

The presence of too little ammonia often results in the formation of black Ni(OH)₂ at the anode; the analysis then comes out too low. Copper, cobalt, and zinc will be deposited under the above conditions.

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[1] Cf. p. 194.

3. Determination as Nickelous Oxide

Heat the nickel solution in a porcelain dish with bromine water and an excess of pure potassium hydroxide; the nickel is precipitated as brownish black nickelic hydroxide, $Ni(OH)_3$. Filter off the precipitate, wash by decantation with hot water, dry, and, after burning the filter, heat strongly and weigh as NiO. The grayish green oxide thus obtained always contains small quantities of silicic acid and alkali,[1] so that the results are too high. By treating the ignited mass with hot water, the greater part of the alkali can be removed. Drying and again igniting gives the weight of $NiO + SiO_2$. Treat the oxide in a porcelain crucible with hydrochloric acid, evaporate to dryness, moisten the dry residue with concentrated hydrochloric acid and then with hot water, filter through a small filter, wash with hot water, and ignite the filter together with the residue in a platinum crucible. The weight of this silica, SiO_2, subtracted from the former weight of $NiO + SiO_2$ gives good results.

Remark. It is possible to precipitate nickel quantitatively as $Ni(OH)_2$ by means of caustic potash alone and the precipitate can be changed to NiO by ignition. This method is open to the same objections as the above and, furthermore, $Ni(OH)_2$ is not so easily filtered and washed as $Ni(OH)_3$.

These two methods are more tedious to carry out and since the results are not as accurate as those of the first two methods described they will probably not be used much in the future.

Besides the methods described, it has been proposed to precipitate nickel as the sulfide, and weigh it as the oxide by ignition in air [2] The method is good but hardly comparable with the dimethylglyoxime method, the electrolytic method, or the volumetric titration with potassium cyanide.

COBALT, Co.   At. Wt. 58.94

Forms: Co, $CoSO_4$, $Co(C_{10}H_6ONO)_3$

1. Determination as Metal

(a) By Electrolysis

The most accurate method for the estimation of cobalt is by electrolysis, and the details of the process are precisely the same as have been given under " Nickel," i.e., from a strongly ammoniacal solution

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[1] Cf. A. Windelschmidt, *Dissertation*, Münster, 1907, and W. D. Treadwell, *Dissertation*, Zürich, 1909

[2] H Cormimboef, *Ann. chim. applicata*, II, 6 (1906). Cf. A. Windelschmidt, *loc. cit.*

containing ammonium salts and the sulfate or chloride (preferably the sulfate) of cobalt. It is customary to use a little more ammonia than in the determination of nickel, because cobalt has a greater tendency to deposit as black Co(OH)₃ at the anode. The duration of the electrolysis is the same as with nickel, rather than somewhat longer. At the end of the determination, after the electrodes have been removed, test the entire solution for cobalt by boiling off ammonia, making acid with a little acetic acid, and adding 5 ml of water which has been saturated with H_2S. Compare the color with that produced similarly with known quantities of cobalt. Make a corresponding correction to the weight of cobalt obtained by electrolysis.

(b) By Reduction of the Oxide in a Stream of Hydrogen

Heat the cobalt solution to boiling in a porcelain evaporating dish, and precipitate the cobalt as black cobaltic hydroxide by the addition of caustic potash and bromine water. Filter off the precipitate,[1] dry, and ignite. Then cool and treat the oxides with water to remove the small quantity of alkali which is always present. Filter, ignite in a stream of hydrogen, and weigh as metal. After weighing, dissolve the metal in hydrochloric acid, evaporate the solution to dryness, moisten the dry mass with hydrochloric acid, treat with water, and filter off the small residue of silicic acid. Ignite this residue and subtract its weight from that obtained after the ignition in hydrogen. Cobalt may also be precipitated as cobaltous hydroxide by caustic potash alone, but the resulting precipitate is not as easy to filter and wash as the cobaltic hydroxide. Precipitation by means of sodium carbonate is not so satisfactory.

The oxides of cobalt when ignited in air yield a mixture of CoO and Co_3O_4 in varying proportions, so that they are not suited for the quantitative determination of cobalt.

Remark. The results obtained by this method are usually a little higher than those by electrolysis.

2. Determination as Sulfate

The method is the same as was described under "Manganese" (p. 188).

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[1] Cobaltic hydroxide, unlike nickelic hydroxide, tends to yield a turbid filtrate on washing. A good grade of ashless filter paper is required.

3. Determination with α-Nitroso-β-naphthol, $C_{10}H_6(NO)OH$

α-Nitroso-β-naphthol, ⬡⬡ with NO and OH, precipitates Cu, Cr, Zr, Ti, V, Sn, W, Pd, Fe,
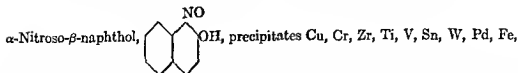
and Co and does not precipitate Sb, Al, Mg, Ni, Zn, Mn, Ca, Sr, or Ba. If an excess of cobaltous salt is added to a neutral, aqueous solution of the sodium salt of α-nitroso-β-naphthol, a brownish red precipitate of $Co(C_{10}H_6NO_2)_2$ is obtained, but by heating with acids this cobaltous compound is converted into the more stable trivalent cobaltic salt $Co(C_{10}H_6NO_2)_3$ by atmospheric oxidation. This is analogous to the oxidation of $K_4Co(CN)_6$ to $K_3Co(CN)_6$. The corresponding nickelous compound is brownish yellow. It is not very soluble in water or dilute acetic acid but it dissolves readily in dilute hydrochloric or sulfuric acid. The most important applications of the reagent α-nitroso-β-naphthol in analytical chemistry are for the detection of small quantities of cobalt and for the determination of cobalt¹ in the presence of large quantities of nickel. A solution of the reagent in 50 per cent acetic acid is added to the solution of nickel and cobalt and the solution is made acid with hydrochloric acid. The brick-red precipitate is heated strongly in the air and weighed as Co_3O_4 or, better, reduced to metallic cobalt in hydrogen and weighed as Co.

Procedure. To the neutral solution containing 1 to 30 mg of Co and not more than 0.2 g of nickel, add 5 ml of concentrated HCl and dilute to 200 ml. Heat to about 80°, and add slowly while stirring an excess of the reagent which is freshly prepared by dissolving 2 g of the organic compound in 75 ml of glacial acetic acid, diluting the solution with 75 ml of water, and filtering. Use 15 ml of the reagent for each milligram of Co. After 3 or 4 hours filter through a filtering crucible; wash with cold water, then with hot 1.5 N HCl, and finally with hot water till free from acid and nickel. Dry the precipitate, sprinkle a little powdered oxalic acid over it to prevent too sudden combustion, and heat in a good oxidizing atmosphere to about 1000°. Weigh as Co_3O_4.

If the precipitate is large, ignite it in hydrogen and weigh as Co or filter it through a paper filter, destroy organic matter by heating with sulfuric and nitric acids, and then determine cobalt by one of the other methods.

To accomplish the destruction of organic matter, add 10 ml of concentrated HNO_3 and an equal volume of concentrated H_2SO_4. Evaporate in a porcelain or platinum dish, and heat until fumes of H_2SO_4 escape freely. This causes a blackening of the acid solution. Cool, add 5 ml more of concentrated HNO_3, and again evaporate till dense fumes are evolved. Continue this treatment until the solution does not darken when it is evaporated to fumes of H_2SO_4.

¹ Ilinsky and Knorre, *Ber.*, **18**, 699 (1885); G. v. Knorre, *Z. angew. Chem.*, **17**, 677 (1904). See also Schmidt, *Z. anorg. allgem. Chem.*, **80**, 335 (1913); Krauss and Dencke, *Z. anal. Chem.*, **67**, 86 (1925); C. Mayr, *Z. anal. Chem.*, **98**, 402 (1934).

ZINC, Zn. At. Wt. 65.38

Forms: $ZnNH_4PO_4$, $Zn_2P_2O_7$, ZnO, ZnS, Zn

1. Determination as Zinc Ammonium Phosphate or Zinc Pyrophosphate

This excellent method, first recommended by H. Tamm,[1] has been studied and improved by G. Lösekann and T. Meyer,[2] M. Austin,[3] and especially H. D. Dakin.[4]

Procedure. To the *cold*, acid solution of the zinc salt add ammonium hydroxide until the solution is barely acid to methyl orange. Care is necessary at this point, as zinc ammonium phosphate is soluble both in acids and in ammonia. Dilute with water to a volume of 150 ml, and heat on the water bath. To the hot solution, add 10 times as much ammonium phosphate by weight as there is zinc present. (If the diammonium phosphate contains monammonium phosphate, the salt should be dissolved in cold water and dilute ammonia added until the solution just becomes pink with phenolphthalein.) The precipitate that first forms is amorphous but it soon changes into fine crystals of zinc ammonium phosphate. The transformation takes place more rapidly in proportion to the quantity of ammonium salts present. After the heating has continued for about 15 minutes, remove the dish from the water bath, and after the precipitate has settled for a short time filter it off into a weighed filtering crucible, wash with hot 1 per cent ammonium phosphate solution until free from chloride, etc., then twice with cold water, and finally with 50 per cent alcohol. Dry at 100–135° for an hour and weigh as $ZnNH_4PO_4$ which contains 36.64 per cent Zn. The precipitate can be washed and dried with alcohol and ether if desired (cf. p. 83).

Or the precipitate may be weighed as the pyrophosphate, $Zn_2P_2O_7$, in which case it is desirable to heat the dried zinc ammonium phosphate very slowly in an electric oven to 900–1000°. If such an oven is not at hand place the filtering crucible in a larger crucible and heat over the gas flame. Gradually raise the temperature until finally the full heat of the Teclu or Méker burner is reached. Heat to constant weight. $Zn_2P_2O_7$ contains 42.90 per cent Zn.

Test the filtrate from the $ZnNH_4PO_4$ precipitate with ammonia and ammonium sulfide. If a small precipitate of white zinc sulfide is formed, filter it off, using a paper filter, ignite in a porcelain crucible, and weigh

[1] *Chem. News*, 24, 148.
[2] *Chem. Ztg.*, 1886, 729.
[3] *Am. J. Sci*, 1899; *Z. anorg. Chem.*, 22, 212 (1900).
[4] *Z. anal. Chem.*, 39, 273 (1900).

as ZnO. No sulfide precipitate will be formed if the above conditions were followed carefully.

The determination as pyrophosphate is to be recommended when the zinc solution contains a very large quantity of ammonium salts because long washing is required to remove them and this renders the results a little low. When the precipitate is weighed as pyrophosphate, the ammonium salts are volatilized and it is not necessary to remove them by washing. If the precipitate is very gelatinous, $AlPO_4$ is probably present.

Remark. Under some conditions, as when magnesium or aluminum is present, the procedure of K. Voigt is followed. To the solution of the zinc salt, containing ammonium salts as well, add an excess of ammonia and the required volume of ammonium phosphate solution. After allowing to stand for some time, filter off the precipitated magnesium ammonium phosphate and aluminum phosphate; the zinc ammonium phosphate is soluble in ammonia. Heat the filtrate on the water bath until all the free ammonia has been expelled, whereby zinc ammonium phosphate separates quantitatively in the form of the crystalline precipitate. Treat this precipitate as described above. If some of the precipitate should adhere firmly to the sides of the dish, it may be dissolved in a few drops of hydrochloric acid, the solution immediately neutralized with ammonia, and heated a few minutes on the water bath before filtering.

2. Determination as Zinc Oxide

The carbonate, nitrate, acetate, and oxalate of zinc are readily and quantitatively changed to zinc oxide by ignition in the air; the sulfate, when present in relatively large amounts, is transformed into oxide with difficulty. Small amounts of the sulfate may be changed to oxide by igniting over the blast lamp. It is advisable, however, if the zinc is present as sulfate, to precipitate it from the aqueous solution as sulfide and weigh it as such according to 3; or to dissolve the sulfide on the filter in dilute hydrochloric acid, receiving the solution in a weighed platinum dish, evaporate to dryness on the water bath, change to oxide by the method of Volhard as described below, and weigh as such.

The chloride is readily changed to oxide, according to Volhard, by gentle ignition with pure mercuric oxide. The method is as follows: Treat the neutral solution of the chloride, contained in a platinum dish, with a large excess of pure yellow mercuric oxide,[1] suspended in water, and evaporate to dryness on the water bath; mercuric chloride and

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[1] The mercuric oxide is prepared by precipitating a solution of mercuric chloride with pure caustic potash. Allow the precipitate to settle, wash by decantation with water until free from chloride, and keep suspended in water in a bottle with a wide neck. A considerable amount of the mercuric oxide, say 5–10 g, should leave no weighable residue after ignition.

zinc oxide are formed

$$ZnCl_2 + HgO = ZnO + HgCl_2$$
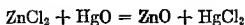
both of which are white substances. Enough mercuric oxide should be used so that the residue obtained after the evaporation is noticeably yellow.

Ignite the dry mass under a hood with a good draft (on account of the poisonous mercury vapors), at first gently and finally strongly, and weigh the residue of zinc oxide; both mercuric chloride and oxide are volatile. The results are excellent.

If the solution contains alkalies as well as zinc, the zinc can be precipitated as basic carbonate and changed to oxide upon ignition. The precipitation of the zinc carbonate should take place in a porcelain dish, and the sodium carbonate solution should be added drop by drop to the cold, barely acid solution free from ammonium salts.[1] Add the sodium carbonate solution until the zinc solution becomes turbid, then heat to boiling; the greater part of the zinc is precipitated as granular zinc carbonate. Add 2 drops of phenolphthalein indicator solution and enough sodium carbonate solution to impart a distinct pink color. In this way a precipitate of zinc carbonate is obtained free from alkali, which is not the case if the hot solution is at once precipitated by the addition of an excess of sodium carbonate.[1] Filter the precipitate from the *hot* solution and wash with hot water until 20 drops of the filtrate leave no residue on evaporation. Dry the precipitate, transfer the greater part to a weighed porcelain crucible, burn the filter by itself in a platinum spiral, and add the ash to the main part of the precipitate in the crucible. Ignite at first gently and finally strongly over a Teclu or Méker burner, and weigh[2] after cooling in a desiccator.

If the zinc solution contains ammonium salts, it is possible to remove them by boiling with an excess of sodium carbonate solution.

3. Determination as Sulfide

This determination is chosen when the zinc is present in a solution containing ammonium salts, or when it is necessary to separate zinc from alkaline earths, alkalies, or metals of this group. Zinc sulfide may

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[1] If considerable amounts of ammonium salts are present there may be no precipitation. Sodium carbonate should then be added until the solution is slightly alkaline and the solution boiled until all the ammonia is expelled.

[2] If the solution contains sulfate, the precipitate produced by sodium carbonate always contains more or less basic zinc sulfate, which may easily lead to high results. In the presence of sulfates, therefore, it is advisable to precipitate the zinc as sulfide and determine it as such according to 3.

be precipitated from ammoniacal solutions, or from solutions containing free acetic, formic, citric, or thiocyanic acids in the presence of ammonium salts.

(a) Precipitation of ZnS from Ammoniacal Solutions

Place the slightly acid solution in an Erlenmeyer flask and treat with sodium carbonate solution until a permanent precipitate is obtained. Dissolve this by the addition of a few drops of ammonia, and then, for every 100 ml of the solution, add 5 g of ammonium acetate (or, better ammonium thiocyanate), followed by a slight excess of freshly prepared ammonium sulfide. Nearly fill the flask with boiled water, stopper, and allow to stand 12 to 24 hours. Without disturbing the precipitate, pour the clear supernatant liquid through a paper filter of fine texture. Cover the precipitate with a 5 per cent solution of ammonium acetate (or ammonium thiocyanate) containing 2 ml of ammonium sulfide solution. Shake, allow to settle, and pour the turbid solution through the filter, taking care to receive the filtrate in a fresh beaker; if it comes through turbid pour it through the filter again. Repeat the decantation 3 times, after which transfer the precipitate to the filter and wash completely with the above wash liquid, taking pains to keep the filter full during the entire operation, finally washing with water containing ammonium sulfide only. Dry the precipitate, transfer as completely as possible to a weighed Rose crucible, burn the filter by itself, and add the ash to the main portion of the precipitate. Mix the precipitate with one-third as much pure sulfur, cover with a layer of sulfur, and heat as described under "Manganese" (p. 191), in a current of hydrogen. Finally allow the crucible to cool in the stream of hydrogen and weigh the zinc sulfide.

(b) Precipitation of ZnS from Acid Solutions

To the solution, which has been nearly neutralized with ammonia, add ammonium chloride or sulfate as in the previous method and a little ammonium or sodium acetate; then saturate with hydrogen sulfide. After the precipitate has settled completely, pour the supernatant solution through a filter, and wash the precipitate with 2 to 4 per cent acetic acid which has been saturated with hydrogen sulfide. When thoroughly washed, treat as described above. It is to be noted that the zinc sulfide shows less tendency to form colloidal solutions when it is thrown down from a slightly acid solution than when it is precipitated from alkaline solutions.

4. Electrolytic Determination of Zinc

It is possible to deposit zinc electrolytically with a current of 0.2–0.3 ampere from a neutral solution to which sodium acetate and a few drops of acetic acid have been added. From the solution of potassium or sodium zincate, or from the complex alkali zinc cyanides, it is easier to deposit the zinc quantitatively.

(a) Method of F. Spitzer[1]

To the solution of zinc sulfate (chlorides and nitrates should be absent) add a drop of phenolphthalein and sodium hydroxide solution until a permanent coloration is obtained. Then add 20–25 ml of 4 N sodium hydroxide solution, dilute to 150–200 ml, and electrolyze with a current of 0.8–1 ampere and 3–4 volts electrode potential using a platinum gauze cathode. At the end of 3 hours the electrolysis is finished, provided that not more than 0.5 g of zinc was present. Without breaking the current, raise the electrodes nearly out of the bath, wash the upper portions quickly with water, then remove the electrodes entirely from the solution and rinse with water. Turn off the current, wash the cathode with alcohol, dry over a flame, cool in a desiccator, and weigh. Under these conditions, zinc forms a bluish gray deposit that adheres firmly to the electrode. To make sure that all the zinc was deposited, clean the electrodes and electrolyze the solution for 30 minutes longer. A slight increase in weight will always be obtained because the anode is attacked slightly by the alkaline solution so that the cathode slowly continues to gain in weight from deposited platinum. If at the end of half an hour the gain in weight is not over 0.3 mg then the deposition of the zinc was complete the first time, as can be shown by testing with hydrogen sulfide. The results are always a little high.[2]

To clean the electrodes, boil them with 4 N hydrochloric acid, wash well with distilled water, and heat over a flame. It is not necessary to cover the platinum gauze with a thin coating of copper or of silver, as has been recommended when a platinum dish is used as the cathode.

Remark. If too little caustic soda is present, a spongy deposit of zinc is obtained which does not adhere well to the electrode. For this reason the above directions should be followed closely.

[1] Z. Elektrochem., 11, 401 (1905).
[2] Ellwood B. Spear, J. Am. Chem. Soc., 32, 530 (1910). The experiments have been repeated in the Zürich laboratory by Janini, who obtained as an average from fourteen determinations with 50 ml of a zinc sulfate solution the value 0 1014 g Zn instead of 0.100S g Zn, a difference of about 0.6 per cent.

In the presence of ammonia the determination is not successful. Therefore, if it is desired to analyze a solution containing an ammonium salt, it must be boiled with caustic soda until all the ammonia has been expelled. Moreover, if chlorides or nitrates are present they must be removed by evaporation with sulfuric acid. Evaporate the solution on the water bath and finally heat over the free flame until dense vapors of sulfuric acid are expelled. Dilute the solution and electrolyze as described.

(b) The Potassium Cyanide Method[1]

Add a drop of phenolphthalein indicator to the solution of zinc sulfate, caustic soda until a permanent pink coloration is obtained, and then potassium cyanide until a clear solution results. Dilute to a volume of 150–200 ml and electrolyze with a current of 0.2–0.3 ampere. At first the electrode potential is about 5.8 volts, but it falls during the analysis on account of the current heating the solution. The electrolysis is finished in 2 or 3 hours.

SEPARATION OF MANGANESE, NICKEL, COBALT, AND ZINC FROM THE ALKALINE EARTHS

The separation depends upon the insolubility of the sulfides of the metals of this group and the solubility of the sulfides of the alkaline earths.

Procedure. Treat the neutral solution of the chlorides in a 250-ml Erlenmeyer flask with ammonium chloride (if it is not already present), and add 2 ml of concentrated NH_4OH. Saturate with H_2S, which causes precipitation of sulfides and formation of NH_4HS. Add 2 ml more of concentrated ammonia to form $(NH_4)_2S$, dilute to the neck of the flask with recently boiled water, stopper, and let stand for several hours. Filter uninterruptedly through paper, and wash with cold 2 per cent NH_4Cl solution. Keep the funnel covered as much as possible. Any green color of the filtrate indicates lack of sufficient precipitant or electrolyte.

If only a small quantity of alkaline-earth metals is present and the ammonium sulfide solution is entirely free from ammonium carbonate, the separation is usually complete after one precipitation; in the presence of considerable calcium, strontium, barium, or magnesium the sulfide precipitate will always be more or less contaminated with these substances, so that the precipitation must be repeated. For this purpose transfer the washed precipitate as completely as possible to a porcelain crucible, burn the filter paper in a platinum spiral, and add

[1] Luckow, *Z. anal. Chem.*, **19**, 1 (1880); Beilstein and Jawein, *Ber.*, **12**, 446 (1879); Milot, *Bull. soc. chim.*, **37**, 339 (1882); W. D. Treadwell, *Elektroanalyt. Methoden.*

the ash to the main part of the precipitate. Cover the crucible with a watch glass, add 2 N hydrochloric acid, and heat gently after the evolution of hydrogen sulfide has ceased, to remove all dissolved gas. Now add a little concentrated nitric acid and heat the mixture until the precipitate is completely dissolved and the solution is evaporated to dryness, add a little concentrated hydrochloric acid, and again evaporate to make sure that no nitrate remains. Moisten the dry mass with a few drops of concentrated hydrochloric acid, dissolve in hot water, and filter off the slight residue of sulfur, which, if barium is present, always contains a small amount of barium sulfate. Wash the residue with hot water, dry, ignite in a porcelain crucible, and weigh. Treat the filtrate exactly as before with ammonium sulfide.

If nickel is present, an excess of ammonium sulfide must be carefully avoided, as otherwise some nickel sulfide will pass through the filter (cf. Vol. I). Always, however, the filtrate should be tested for nickel by acidifying with acetic acid, heating to boiling, and passing hydrogen sulfide into the solution. If a slight black precipitate is produced by this treatment, filter it off and combine with the main precipitate (cf. pp. 215 *et seq.*). Free the filtrate, containing the alkaline-earth cations, from ammonium salts by evaporating to dryness and heating the residue; dissolve this in hydrochloric acid, and examine as described on pp. 249 *et seq.*

Remark. Solutions of NH_4OH absorb CO_2 from the air and form ammonium carbonate which precipitates the alkaline earths. It is best to use ammonia which has been freshly distilled with lime. If nickel and cobalt are absent, the sulfide precipitate should dissolve easily in hot, dilute HCl, and the above-described heating in a crucible followed by treatment with nitric acid is unnecessary.

Preparation of Ammonia Free from Carbonate and Silicate

Add 10 g of freshly slaked lime to 500 ml of concentrated ammonia contained in a liter flask that is connected with a condenser. Close the condenser by means of a tube containing soda-lime, and allow the contents of the flask to stand for a day with frequent shaking. Then place 300–400 ml of water in a flask and boil, meanwhile passing through the water a current of air that has been freed from all traces of carbon dioxide by passing through concentrated caustic potash solution and then through a tower filled with soda-lime. Allow the water to cool in this air stream. Place the flask containing the ammonia on the water bath in such a position that the condenser tube is inclined slightly upward, and connect this with the delivery tube, through which the air previously passed into the flask of boiling water. By heating the water bath, distil the ammonia over into the flask containing the boiled water, by which it is completely absorbed. By saturating a part of this ammonia with hydrogen sulfide, a solution of ammonium sulfide is prepared suitable for the above-described separation.

SEPARATION OF THE BIVALENT FROM THE OTHER METALS OF THE AMMONIUM SULFIDE GROUP

This separation is often designated as that of the *protoxides* from the *sesquioxides*; this designation is not applicable with respect to quadrivalent titanium and zirconium, etc , or to sexivalent uranium which are often precipitated with the trivalent ions. The Latin prefix *sesqui* means *one and a half times*; the prefix *proto* is derived from the Greek and means *first* or *lowest of a series*. Oxides of the general formula MO (in our present nomenclature) are the *protoxides*, and oxides of the general formula M_2O_3 are the *sesquioxides*. According to the dualistic theory of Berzelius, salts were considered combinations of metal oxides with non-metallic oxides, and compounds such as $NaCl$ and $AlCl_3$ were not regarded as salts but as *binary* compounds formed from only two elements. The analytical chemist still reports his results in terms of the oxides, and, even today, the older chemists think of the oxidation of a ferrous salt by permanganate as the oxidation of FeO to Fe_2O_3 by means of Mn_2O_7 and balance their equations of oxidation and reduction on this basic assumption.

Insoluble hydroxides or basic salts of trivalent iron, chromium, and aluminum and of quadrivalent titanium and zirconium precipitate when the acidity of the solution lies between 10^{-4} and 10^{-7} ⁶ mole of hydrogen ions per liter. Bivalent uranyl ions usually precipitate also at this acidity.

It is quite common to express the acidity of a solution in terms of the so-called *hydrogen exponent*, pH, which is the value log 1/*c* when *c* is the concentration of H^+ in moles per liter. Thus a concentration of 10^{-6} mole of hydrogen ions per liter is expressed briefly by saying pH = 6. Since the logarithm to the base 10 of 1 is 0 and the logarithm of a fraction is the logarithm of the numerator minus the logarithm of the denominator, it is evident that log 1/*c* = 6 when *c* = 10^{-6}.

It is easy to tell when the hydrogen-ion concentration corresponds approximately to pH = 5 because methyl red indicator in dilute solution changes from red to yellow at this point. Most methods for separating ions of iron, chromium, and aluminum from the bivalent ions of the third group depend upon the neutralization of an acid solution. This may be accomplished by the careful addition of ammonia, by adding a salt of a weak acid, or by adding an insoluble carbonate or oxide. Theoretically, the separation could be accomplished by the addition of caustic alkali or alkali carbonate provided that the solution was never allowed to become more alkaline than corresponds to pH = about 5, but it is practically impossible, because some portion of the solution is likely to contain a slightly lower acidity, even although it is well stirred, and the excess of this causes the precipitation of insoluble hydroxides of bivalent metals. It is difficult to make the separation with ammonium hydroxide, for this same reason, but when ammonium hydroxide is added to a solution containing an ammonium salt, its ionization is repressed so that it amounts to less than one-hundredth as much as that of a caustic alkali solution of the same normal concentration Moreover, in ammonium hydroxide solution, the greater part of the reagent consists merely of dissolved NH_3 and this forms complex ions with many bivalent ions, particularly copper, cadmium, nickel, cobalt, and zinc ions, and the formation of these complexes prevents precipitation of hydroxides.

The Barium Carbonate Method

This method depends upon the fact that ferric, aluminum, and chromic ions (as well as titanic, zirconic, and uranyl ions) are precipitated in the cold by barium

carbonate, whereas the bivalent manganese, nickel, cobalt, zinc, and ferrous ions are not. Salts of the trivalent metals undergo hydrolysis when in dilute aqueous solution:

$$Fe^{+++} + HOH \rightleftharpoons Fe(OH)^{++} + H^+$$
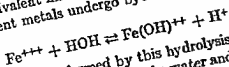
Free acid and a basic salt are formed by this hydrolysis; the composition of the product formed depends upon the quantity of the water and the temperature. If the free acid is removed by the addition of barium carbonate, the equilibrium is disturbed and the hydrolysis goes farther until finally the insoluble hydroxide is formed:

$$Fe(OH)^{++} + 2HOH \rightarrow Fe(OH)_3 + 2H^+$$
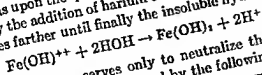
The barium carbonate, then, serves only to neutralize the acid set free by the hydrolysis, and the total reaction is expressed by the following equation:

$$2Fe^{+++} + 3HOH + 3BaCO_3 \rightarrow 3Ba^{++} + 2Fe(OH)_3 + 3CO_2 \uparrow$$
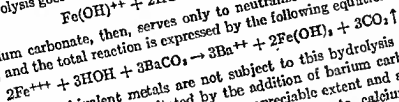
The salts of the bivalent metals are not subject to this hydrolysis *in the cold*; consequently they are not precipitated by the addition of barium carbonate. On warming, however, they are hydrolyzed to an appreciable extent and are then precipitated by barium carbonate. Instead of barium carbonate, calcium carbonate, cadmium carbonate, lead carbonate, zinc oxide, magnesium oxide, and mercuric oxide are sometimes used. Aqueous suspensions of the insoluble oxides or carbonates are commonly used. The barium carbonate suspension can be obtained by mixing aqueous solutions of 36 g Na₂CO₃ and 90 g BaCl₂·2H₂O, allowing the precipitate to settle and decanting off the dilute solution which contains the excess BaCl₂ and NaCl. Similarly the suspension of mercuric oxide can be made by pouring a hot solution of mercuric chloride (about 30 g per 100 ml) into an excess of hot 10 per cent sodium hydroxide (free from iron). The pH values of the various suspensions are: HgO = 6, PbCO₃ = 6.2, CdCO₃ = 6.5, BaCO₃ = 7.3, CaCO₃ = 7.4, MgCO₃ = 9.5.

Procedure. Add sodium carbonate solution, drop by drop, to the slightly acid solution of the chlorides or nitrates, but not the sulfates¹ of the metals, in an Erlenmeyer flask until a slight, permanent turbidity is produced; redissolve this by the addition of a few drops of dilute hydrochloric acid. Dilute the solution and add pure barium carbonate² (suspended in water) until, after thorough shaking, an excess of the carbonate remains on the bottom of the flask. Stopper the flask and ~~~~ to stand for several hours with frequent shaking. Then decant ~~~~~ liquid through a filter, treat the residue in this way, transfer decant. Wash the precipitate 3 times in this way, transfer ~~pite to the filter, and wash thoroughly on the filter with er. The precipitate contains all the iron, aluminum, chromium, and uranium in the presence of the excess of barium ~~te. The filtrate contains the bivalent metals and barium

¹ium carbonate will precipitate the bivalent metals when sulfates are present,

$$ZnSO_4 + BaCO_3 = ZnCO_3 + BaSO_4$$

he barium carbonate must be free from alkali carbonate.

Dissolve the precipitate in normal hydrochloric acid solution, boil to remove carbon dioxide, and separate the iron, aluminum, chromium (titanium and uranium) from the barium[1] by double precipitation with ammonium sulfide as described on p. 205. Separate the iron, aluminum, chromium (titanium, zirconium, and uranium) from one another as described on pp. 167–188.

In the filtrate from the barium carbonate precipitation remove barium by the addition of sulfuric acid[2] to the boiling solution after it has been made acid with hydrochloric acid. Filter off the barium sulfate and separate the bivalent cations from one another as described on pp. 215–219.

Remark. The above separation of the sesquioxides from the protoxides is not absolutely certain in the presence of nickel and cobalt. In this case, particularly when considerable iron is present, the precipitate produced by barium carbonate contains a little nickel and cobalt. This difficulty can be overcome, however, by adding ammonium chloride to the solution (3–5 g for each 100 ml of solution) before precipitating with barium carbonate; the separation is then satisfactory.

SEPARATION OF IRON, ALUMINUM, AND TITANIUM (BUT NOT CHROMIUM AND URANIUM) FROM MANGANESE, NICKEL, COBALT, AND ZINC

Basic Acetate Method

This classic method depends upon the fact that ferric, aluminum, and titanium acetates are hydrolyzed in hot, dilute solutions much more readily than the acetates of the bivalent metals. From the equation

$$Fe(C_2H_3O_2)_3 + 2HOH \rightleftarrows 2HC_2H_3O_2 + Fe(OH)_2 \cdot C_2H_3O_2$$

it is evident that acid is set free which tends to stop the reaction, owing to the solvent action of hydrogen ions. The concentration of free hydrogen ions, however, is kept low by the addition of sodium acetate. Then, as a rule, some manganese is likely to be precipitated, so that it is advisable to dissolve the precipitate and repeat the precipitation. Hydrated manganese dioxide, $MnO_2 \cdot H_2O$, or manganic hydroxide, $Mn(OH)_3$, is more insoluble than mangannus hydroxide, $Mn(OH)_2$, and hence long boiling in the air tends to increase the quantity of manganese precipitated. The method is somewhat tedious but gives excellent results.

Procedure. To the slightly acid solution of the *chlorides*, contained in a small beaker, add sodium carbonate solution in the cold until a slight permanent opalescence is obtained; redissolve the precipitate

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[1] Most authorities recommend precipitating the barium first with sulfuric acid and then separating the iron, aluminum, etc. Since the precipitate of barium sulfate always contains small amounts of the heavy metals, the above procedure is preferable.

[2] Or, better, by double precipitation of the other metals with ammonium sulfide.

by the addition of a few drops of dilute hydrochloric acid. Meanwhile prepare a boiling, dilute solution of sodium or ammonium acetate in a large round-bottomed flask, containing, for each 0.1–0.2 g of iron or aluminum, 1.5–2 g of acetate and 300–400 ml of water. When the iron solution is ready, take away the burner from beneath the flask; add the solution of iron, aluminum, etc.; replace the burner; and continue the boiling for 1 minute. Then remove the flame (the precipitate becomes slimy on long boiling), allow the precipitate to settle, and filter while the liquid is hot through a fluted filter, washing three times by decantation with boiling water containing ammonium or sodium acetate. Spread the filter together with the precipitate upon a glass plate, rinse the bulk of the precipitate into a porcelain dish, and dissolve the precipitate remaining on the filter by alternately treating with hot 3 N hydrochloric acid and with hot water. Evaporate the resulting solution nearly to dryness on the water bath and repeat the basic acetate precipitation exactly as before. Dissolve the filtered and washed precipitate in hydrochloric acid and separate the iron from aluminum according to p. 168. To the combined filtrates from the basic acetate precipitation, add 10–20 ml of concentrated hydrochloric acid to prevent the precipitation of hydrated manganese dioxide, evaporate almost to dryness, dilute with a little water, precipitate manganese, nickel, cobalt, and zinc by ammonium sulfide as described on p. 203, and analyze according to p. 215.

Remark. This procedure requires practice. It is especially suited for the separation of iron and titanium from the protoxides; the separation is usually less satisfactory with aluminum, and so if considerable amounts of the latter are present, the barium carbonate separation is to be preferred. If it is merely a case of the

Separation of Iron from Manganese

the following modifications of the basic acetate process give satisfactory separations with only one precipitation.

O. Brunck's Method[1]

To the acid solution, containing not more than 0.3 g of iron, add 0.35 g of potassium chloride or 0.26 g ammonium chloride for each 0.1 g of iron present. Evaporate the solution to dryness on the water bath, break up the residue by pressure with a glass rod, and heat 5 or 10 minutes longer. By this time practically all the mineral acid is expelled. Dissolve the residual salts in 10–20 ml of water, and to the resulting

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[1] *Chem. Ztg.*, 1904, I, 513. Cf. W. Funk, *Z. anal. Chem.*, 45, 181 (1906).

solution add 1.5 g of sodium acetate for each 0.1 g of iron present.[1]
Dilute the solution with boiling water to a volume of 400–500 ml for
each 0.2 g of iron present; heat, with constant stirring, until boiling
begins, then remove the flame and allow the precipitate to settle.
Decant off the solution through a fluted filter and wash the precipitate
with hot water. Dissolve the precipitate in as little hydrochloric acid
as possible, precipitate the iron by ammonia, filter, dry, and ignite as
described on p. 153. Make the filtrate from the basic acetate precipita-
tion, or better the combined filtrates from both precipitations,[2] acid
with hydrochloric acid, evaporate nearly to dryness, dissolve the
deposited salts in a little water, precipitate manganese, nickel, cobalt,
and zinc with ammonium sulfide according to the directions on p. 205,
and separate according to p. 215.

SEPARATION OF IRON AND ALUMINUM FROM MANGANESE, NICKEL, COBALT, AND ZINC

(a) Sodium Succinate Method

This method, applicable for the separation of large quantities of iron from small
quantities of manganese, nickel, etc., is based upon the fact that ferric iron is pre-
cipitated quantitatively from *neutral* solutions as light brown ferric succinate by
the addition of neutral alkali succinate solution, whereas manganese, nickel, etc.,
remain in solution.

Procedure. If the solution contains free acid and all the iron is in
the ferric form, neutralize with ammonia until a reddish brown colora-
tion appears, then add sodium or ammonium acetate until the color
becomes a deep brown. Dilute the solution to at least 200 ml for each
0.1 g of iron present and add 3 g of sodium succinate dissolved in a little
water. Heat nearly to boiling, filter, and wash at first with cold water,
then with warm normal ammonium hydroxide solution, until 20 drops
of the filtrate leave no residue when evaporated to dryness on platinum.
By means of the washing with ammonia, the ferric succinate is changed
to ferric hydroxide. Ignite and weigh as ferric oxide in a porcelain
crucible. If aluminum is present, analyze the ignited residue as de-
scribed on p. 169. The bivalent metals in the filtrate are best precipi-

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[1] The sodium acetate crystals sometimes contain sodium carbonate; they should
be dissolved in a little water and the solution made barely acid with acetic acid
before adding it to the iron solution

[2] To the ammoniacal filtrate from the Fe(OH)₃ precipitate, add 5 ml of concen-
trated hydrochloric acid before adding the solution to the filtrate from the basic
acetate precipitation; otherwise manganese is likely to be precipitated when the
two filtrates are mixed

tated by the addition of ammonium sulfide and analyzed as described on p. 215.

(b) Separation by Ammonia and Ammonium Chloride[1]

To the acid solution containing 5 g of ammonium chloride and not more than 0.2 g of iron and aluminum cations in 200 ml of solution, add a few drops of a 0.2 per cent solution of methyl red in alcohol and heat just to boiling. Carefully add normal ammonium hydroxide solution, drop by drop, until the color of the solution changes to a distinct yellow. Boil 2 minutes and filter promptly. Wash with hot 2 per cent ammonium nitrate solution until free from chloride. The precipitate contains $Fe(OH)_3$, $Al(OH)_3$, $Ti(OH)_4$, and $Zr(OH)_4$ if the corresponding elements are present.

As good a separation of iron and aluminum from manganese is accomplished in this way as by a single basic acetate precipitation. It is advisable to dissolve the precipitate and repeat the precipitation when the precipitate upon ignition is likely to weigh more than 0.1 g or when a 9-cm filter is more than half full of the precipitate.

Remark. Lundell and Knowles showed that iron and aluminum can be separated from manganese and nickel as satisfactorily by this method of precipitation, which is the same as that recommended by Blum for precipitating aluminum, as by the basic acetate or barium carbonate methods. Phosphoric and vanadic acids follow the iron and aluminum and do not affect the separation if sufficient iron and aluminum are present. If more phosphoric acid or vanadic acid is present than is equivalent to the iron and aluminum, the separation fails as does that of the basic acetate or barium carbonate procedure. Under the above conditions, some cobalt, copper, and zinc will precipitate if present, but a fair separation is effected then by increasing the ammonium chloride content. An excess of both ammonia and ammonium chloride gives better results in the separation of iron from copper and zinc, but the precipitation of the aluminum is then less complete.

(c) Separation by Cupferron

The use of cupferron as precipitant for Fe, Cu, Zr, Ti, etc., has already been mentioned (pp. 154, 177). Here four more procedures will be described to illustrate the use of this reagent.

1. Determination of Iron in Manganese Ores

Principle. After effecting the solution of the ore, the iron is precipitated in acid solution by cupferron. The filtrate then contains all the aluminum, chromium, manganese, nickel, cobalt, zinc, and alkaline earths. After the removal of these elements that may be present, by washing the precipitate with cold water, the organic matter is removed and the iron converted into ferric hydroxide by washing the precipitate with ammonia. The precipitate is ignited and weighed as Fe_2O_3.

[1] Lundell and Knowles, *J. Am. Chem. Soc.*, **45**, 676 (1923).

Procedure. Dissolve about 1 g of the finely pulverized ore in concentrated hydrochloric acid, and evaporate the solution to dryness. Moisten the residue with strong hydrochloric acid, dilute with water, boil, and filter. Fuse the residue with sodium carbonate in a covered platinum crucible, and after the fusion, dissolve the melt in water and dilute hydrochloric acid. Evaporate this solution to dryness, and after the removal of the silica in the usual manner, add the filtrate to the main solution. To the cold solution add 50 ml of cupferron reagent in a fine stream down the sides of the beaker, while stirring vigorously. A brownish red, partly amorphous and partly crystalline precipitate of the ferric salt separates out. As soon as a drop of the reagent causes the formation of a snow-white precipitate of nitrosophenylhydroxylamine, all the iron is precipitated. Add a slight excess of the reagent and allow the solution to stand about 10 minutes. Filter through an ashless paper, using gentle suction. If the last particles of the precipitate cling tenaciously to the beaker, add a little ether to loosen them and remove the ether by adding a little boiling water. Wash the precipitate with cold water until the washings are no longer acid to litmus and then with 6 N ammonia to remove the excess of the reagent and form ferric hydroxide. Finally wash the filter once more with cold water. Ignite the precipitate and weigh as Fe_2O_3.

2. Determination of Manganese in Ferromanganese

Dissolve about 1 g of the material in strong hydrochloric acid and fuse the residue with sodium carbonate in a platinum crucible. Heat the melt with water and add alcohol to reduce the manganate to hydrated manganese dioxide. Filter, and dissolve the residue in hydrochloric acid; add this solution to that obtained in the first place. Precipitate iron with cupferron, as in the previous method, but do not add the ammonia washings to the solution. In the filtrate determine manganese as described on pp. 189 and 191.

3. Determination of Nickel and Cobalt in Arsenical Sulfide Ores[1]

Dissolve 1 g of the ore in 20 ml of a saturated solution of bromine in concentrated hydrochloric acid, and evaporate the solution somewhat to volatilize arsenic trichloride. Add 10 ml of 18 N sulfuric acid and evaporate the solution until dense fumes are evolved. Dilute to 500 ml, heat to boiling, and introduce hydrogen sulfide to precipitate the metals of the copper group and any remaining arsenic. In the filtrate precipitate the iron by cupferron as in Method 1, and after evaporating the

[1] H. Nissenson, Z. angew. Chem., 23, 969 (1910).

filtrate until fumes of sulfuric acid are evolved, determine the nickel and cobalt electrolytically according to pp. 194 and 197.

4. Determination of Titanium and Its Separation from Iron, Aluminum, and Phosphoric Acid[1]

Principle. The iron may be reduced completely to ferrous salt by passing hydrogen sulfide into an acid solution, and then, in the presence of tartaric acid which prevents the precipitation of titanium, precipitated as ferrous sulfide in ammoniacal solution. After acidifying and boiling off the hydrogen sulfide, the titanium can be precipitated quantitatively by means of cupferron while the aluminum and phosphoric acid remain in the tartaric acid solution. It is unnecessary to remove the organic matter before igniting the yellow titanium precipitate.

Procedure. To the solution, which should have a volume not greater than 100 ml, add at least four times as much tartaric acid as corresponds to the weight of the oxides of iron, titanium, aluminum, and phosphorus. Neutralize with ammonia, add 3 ml of 18 N sulfuric acid, and introduce hydrogen sulfide until the solution becomes colorless. Unless all the iron is reduced, the subsequent precipitate of iron sulfide will contain some titanium. After the reduction of the iron is complete, add ammonium hydroxide in considerable excess and precipitate the iron as ferrous sulfide by introducing more hydrogen sulfide gas; the solution should remain alkaline to litmus paper. Filter off the ferrous sulfide, and wash with water containing a little colorless ammonium sulfide. To the filtrate, add 40 ml of 18 N H_2SO_4 and expel the liberated hydrogen sulfide by boiling. When this is accomplished, cool the solution to room temperature, dilute to 400 ml, and treat with an excess of 6 per cent cupferron solution, added slowly down the sides of the beaker while the solution is being well stirred. After the precipitate has subsided, test the supernatant liquid by adding more of the cupferron solution. A white precipitate of nitrosophenylhydroxylamine indicates that an excess of the reagent is present, but a yellow turbidity shows that the precipitation of the titanium is incomplete. It is also well to test the filtrate in the same way. Collect the titanium precipitate on filter paper, using gentle suction, and wash 20 times with normal hydrochloric acid solution. Ignite very cautiously in a platinum or quartz crucible until the organic matter is all consumed. Finally, heat to constant weight over a Méker burner and weigh as TiO_2.

Other Determinations with Cupferron

Zirconium can be precipitated quantitatively from solutions containing as much as 40 per cent of concentrated sulfuric acid by volume, and the presence of tartaric

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[1] W. M. Thornton, Jr., *Am. J. Science*, **37**, 407 (1914).

acid has no effect upon the precipitation. The ignited precipitate is ZrO_2. Thorium, on the other band, is not precipitated quantitatively in the presence of sulfuric acid but can be thrown down from acetic acid solutions. Vanadium, in either the quadrivalent or quinquevalent condition, can be determined quantitatively by precipitation in 1 per cent bydrochloric or sulfuric acid solution provided that the precipitate is washed with 1 per cent acid containing cupferron Tantalum and columbium are also precipitated.

Lead, silver, mercury, tin, bismuth, cerium, and tungsten, interfere more or less with cupferron determinations and are likely to precipitate to some extent in most of the methods that have been described

SEPARATION OF THE BIVALENT METALS OF THE AMMONIUM SULFIDE GROUP FROM ONE ANOTHER

Separation of Zinc from Nickel, Cobalt, and Manganese

Most methods for this separation depend upon the slight solubility of zinc sulfide and the greater solubility of the other sulfides[1] in their state of formation.

It was shown in Vol. I that the solubility products of ZnS, NiS, CoS, FeS, Fe_2S_3, and MnS are all so small that these substances are precipitated quantitatively whenever the corresponding cations come in contact with any appreciable concentration of sulfide ions, as by adding a solution of ammonium sulfide. It was also shown in Vol. I that hydrogen sulfide is a weak acid and only slightly ionized. By adding acid, the concentration of the sulfide ion diminishes in proportion to the square of the concentration of hydrogen ions. Thus, if to an aqueous solution of hydrogen sulfide, enough acid is added to increase the hydrogen-ion concentration tenfold, the concentration of the sulfide ion is diminished to about one one-hundredth of its former value

In a liter of water saturated with hydrogen sulfide at 25°, there is present about 0.1 mole of undissociated hydrogen sulfide, 0.9×10^{-4} mole of hydrogen ions, and only 1.2×10^{-15} mole of sulfide ion. In the saturated solution the relation $[H^+]^2 \times [S^{--}] = 1.1 \times 10^{-22}$ always holds at 25°, according to theory, and, therefore, it is easy to fix the concentration of the sulfide ion by regulating the concentration of the hydrogen ion

Thus, to take a concrete case, suppose a solution to contain 0.2 g of zinc ions and 0.2 g of ferrous ions in 400 ml of solution What concentration of hydrogen ions is necessary to effect a quantitative separation of zinc and iron by hydrogen sulfide? Let us assume that the separation can be called quantitative when all but about 0.5 mg of zinc is precipitated and not over 0.5 mg of iron

The solubility product of zinc sulfide is given in Vol. I as 1.2×10^{-22} and that of ferrous sulfide as 1.5×10^{-19}. Now 0.5 mg of Zn in 400 ml $= \dfrac{0.0005}{65.4} \times \dfrac{1000}{400} = 1.9 \times 10^{-5}$ mole per liter. To reach the solubility product of ZnS it is necessary to have $\dfrac{1.2 \times 10^{-22}}{1.9 \times 10^{-5}} = 6.3 \times 10^{-18}$ mole per liter of S^{--} ions.

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[1] Nickel and cobalt sulfides when once formed are insoluble in dilute acids. These substances probably exist in two allotropic modifications, of which one is soluble and the other insoluble. The soluble form has never been isolated.

The ionization of hydrogen sulfide in a saturated solution is repressed to this value when $[H^+]^2 = \dfrac{1.1 \times 10^{-23}}{6.3 \times 10^{-19}} = 0.17 \times 10^{-4}$ and $[H^+] = 4 \times 10^{-3}$ mole per liter.   A similar computation for FeS shows that the concentration of H^+ ions required to prevent the precipitation of 0.2 g of Fe is about 8×10^{-4} mole per liter.   Therefore, to separate 0.2 g of Fe completely from 0.2 g of Zn in 400 ml of solution it is necessary to keep the concentration of the acid between 8×10^{-4} and 4×10^{-3} mole per liter or, in other words, the solution must be kept between 0.0008 and 0.004 normal in hydrogen ions.

The values for the solubility products given in Vol. I are not accurate enough to predict with certainty whether a definite separation will be accomplished satisfactorily but they indicate the possibility of such separations.   The above computation, therefore, suggests the possibility of separating zinc from iron by means of hydrogen sulfide, and it has been found possible to accomplish this in the laboratory.

To reach the desired concentration of hydrogen ions it is not permissible merely to add just the right quantity of a mineral acid at the start.   During the precipitation of ZnS more hydrogen ions are formed as the following equation shows:

$$Zn^{++} + H_2S = ZnS + 2H^+$$

It is necessary, therefore, to make sure that the acidity is correct when all the zinc is precipitated.   This is more important than the acid concentration at the start, for when hydrogen sulfide is passed into a solution, the least soluble sulfide forms first; and if at one part of the solution a more soluble sulfide forms, it will itself precipitate another less soluble sulfide when it meets the other ion in another part of the solution.

Experimentally, it has been found possible to separate zinc as sulfide from very dilute hydrochloric acid solution after the addition of alkali acetate, and also from a solution containing dilute hydrochloric acid and a large quantity of ammonium salt.   In the latter case it is probable that the ammonium salt exerts a " salting-out effect " and precipitates colloidal zinc sulfide, making the solubility product smaller than it apparently is in pure water.

Method of Cl. Zimmermann[1]

Procedure.   Treat the slightly acid solution with sodium carbonate solution until a permanent precipitate is formed and redissolve by the addition of a few drops of 2 N hydrochloric acid; then for every 80 ml of the solution add 10, or at the most 15, drops of 2 N hydrochloric acid[2] and 10 ml of 20 per cent ammonium thiocyanate solution.   Now heat the solution to about 70° C and saturate with hydrogen sulfide.

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[1] *Ann. Chem. Pharm.*, 199, 3 (1879); 204, 226 (1880).

[2] The addition of hydrochloric acid is always necessary, because otherwise nickel sulfide will be precipitated with the zinc sulfide, especially when considerable nickel and little zinc are present.

At first the solution becomes only slightly turbid,[1] but after some time pure white zinc sulfide is thrown down in clouds, constantly becoming denser. After the solution has become saturated with hydrogen sulfide, cover the beaker and allow it to stand in a warm place until the precipitate has settled and the upper liquid is clear. Then filter and wash the precipitate with 2 per cent NH_4CNS solution which is saturated with H_2S. Weigh either as ZnO or ZnS as described on pp. 201 and 203.

From the filtrate nickel, cobalt, and manganese are precipitated by means of ammonium sulfide, filtered and separated according to the following methods.

Separation of Manganese from Nickel and Cobalt

Treat the solution of the chlorides or sulfates with an excess of sodium carbonate, add a liberal excess of acetic acid, and, for each gram of nickel or cobalt present, introduce 5 g of ammonium acetate. Dilute the solution to 100–200 ml, heat to 70–80° C, saturate with hydrogen sulfide, filter, and wash with hot water. The manganese is in the filtrate, and the nickel and cobalt are in the precipitate.

Remark. The filtrate often contains small amounts of nickel and cobalt. In order to remove these metals, the solution should be evaporated and colorless ammonium sulfide added. Then make slightly acid with acetic acid, warm, and filter. In case a precipitate of nickel or cobalt sulfides is formed by this treatment, test the filtrate in the same way again and repeat the process until no further precipitation is produced.

Separation of Cobalt from Nickel

(a) Method of Tschugaeff-Brunck[2]

This method is probably the quickest and most accurate for the estimation of nickel in the presence of cobalt. It depends upon the fact that nickel is quantitatively precipitated, by means of dimethylglyoxime, from a barely ammoniacal solution or from a slightly acid solution containing sodium acetate. Cobalt, under these conditions, is not precipitated. (See p. 193.) If more cobalt than nickel is present, use two or three times the usual volume of reagent. To determine both nickel and cobalt, divide the solution into two aliquot parts; determine the nickel

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[1] There are at the start but few zinc ions in the solution. The four metals are present for the most part in the form of complex thiocyanates of the general formula $(NH_4)_2[R(CNS)_4]$. The zinc salt, like carnallite (see Vol. I), is slightly dissociated,

$$(NH_4)_2[Zn(CNS)_4] \rightleftharpoons Zn(CNS)_2 + 2NH_4CNS$$
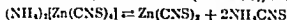
and the zinc thiocyanate is converted into insoluble sulfide by the action of hydrogen sulfide. When the zinc begins to precipitate as sulfide, the equilibrium is disturbed and eventually all the zinc becomes precipitated.

[2] O. Brunck, Z. angew. Chem., 1907 18 45

in one portion with dimethylglyoxime, and in the other portion determine nickel and cobalt together by the electrolytic method (p. 196).

(h) The Potassium Nitrite Method of N. W. Fischer[1]

Brunck's Modification[2]

Evaporate the solution containing an excess of acid to dryness in a porcelain dish and treat the residue with 1 or 2 drops of 2 N hydrochloric acid and 5–10 ml of water. Add pure caustic potash solution, drop by drop, until the reaction is barely alkaline. Dissolve the resulting precipitate in as little glacial acetic acid as possible; add half of the solution's volume of 50 per cent potassium nitrite solution and 10 drops more of acetic acid. Stir the mixture well and allow it to stand 24 hours. At the end of this time the precipitation is almost always complete. This should be proved, however, by removing a little of the undiluted solution with a pipet, adding to it a little more potassium nitrite solution, and allowing to stand a little longer. If at the end of an hour no further precipitation results, then all the cobalt has been precipitated. If a precipitate is formed, add more potassium nitrite to the main solution and again allow to stand. Decant off the clear liquid through a filter, transfer the residue to the filter, and wash with a 10 per cent potassium acetate solution until 1 ml of the filtrate on being acidified with acetic acid and boiled with 1 ml of a 1 per cent solution of dimethylglyoxime will show no test for nickel. This is usually the case after washing 4 times. Transfer as much of the precipitate as possible to a small porcelain dish, cover with a watch glass, cautiously acidify with sulfuric acid, and heat on the water bath until no more brown vapors are evolved. Dissolve the small quantity of precipitate remaining on the filter by pouring hot, dilute sulfuric acid through the filter and add this acid to the main solution of the cobalt. After evaporating as far as possible on the water bath, continue heating on an air bath until dense vapors of sulfuric acid are evolved. After cooling, dissolve the residue in water and determine the cobalt electrolytically, as described on p. 197. If it is not convenient to carry out an electrolysis, dissolve the nitrite precipitate in hydrochloric acid and determine the cobalt according to p. 198 (b).

Remark. This method gives reliable results provided that the solution is free from alkaline earths. If not, the nickel and alkaline-earth metals are precipitated with the cobalt. (Cf. Vol. I.)

1 *Pogg. Ann.*, **71**, 545 (1847).

2 *Z. angew Chem.*, 1907, 1847.

(e) Method of Ilinsky and von Knorre[1]

This method depends upon the fact that cobalt can be precipitated as purple-red $[C_{10}H_6O(NO)]_3Co$ by treatment with α-nitroso-β-naphthol in hydrochloric acid solution. Nickel is not precipitated under these conditions.

Procedure. In one portion determine the cobalt as described on p. 199 and in another determine the nickel with dimethylglyoxime (p. 193).

Separation of Nickel from Zinc. Method of Tschugaeff-Brunck[2]

Treat the solution with ammonium chloride, and add enough ammonia to make slightly ammoniacal; no precipitate should be formed if sufficient ammonium chloride has been added. Make slightly acid with hydrochloric acid, heat to boiling, and precipitate the nickel with an alcoholic 1 per cent dimethylglyoxime solution exactly as outlined on p. 193.

In the filtrate, it is best to precipitate the zinc as sulfide by acidifying with acetic acid and saturating the hot solution with hydrogen sulfide (cf. p. 203).

Remark. When considerable zinc is present it is necessary to add more dimethylglyoxime to precipitate the nickel.

Separation of Nickel from Manganese. Method of Tschugaeff-Brunck[2]

Carry out the analysis exactly as described above except that the final precipitation should take place in an acetic acid solution. Neutralize the greater part of any mineral acid present with ammonia, treat the barely acid solution with 1 per cent dimethylglyoxime solution, and then, after the precipitate has formed, add sodium acetate and continue the analysis according to p. 193. If the alkali acetate is added before the dimethylglyoxime, a very voluminous precipitate is formed which, to be sure, can be filtered with suction, but even then the filtration is tedious. Thus, when possible, it is best to add the sodium acetate *after* the dimethylglyoxime. If, on the other hand, iron has been removed by a basic acetate separation and nickel and manganese are to be determined in the filtrate, the precipitation must take place in a solution already containing sodium acetate. In the filtrate from the nickel dimethylglyoxime precipitation, precipitate the manganese with ammonium sulfide and determine as described on p. 189.

[1] *Ber.*, **18**, 699 (1885)
[2] *Z. angew. Chem.*, 1907, 1849

Separation of Nickel from Iron

If the iron is present in the ferrous condition, oxidize it by boiling with nitric acid. Then dilute to 300 ml, add 1–3 g of tartaric acid, and make the solution ammoniacal to find out whether enough tartaric acid has been added (the solution must remain perfectly clear). Make slightly acid with hydrochloric acid, precipitate the nickel with dimethylglyoxime, carefully neutralize the acid with ammonia, and continue the analysis according to p. 193.

Determination of Nickel in Steel[1]

Procedure. Dissolve 0.5 of steel in 20 ml of 6 N hydrochloric acid. To the resulting solution add 5 ml of concentrated nitric acid and boil 2 minutes to oxidize iron. Dilute to 100 ml, and filter if there is any perceptible residue. Add 3 g of tartaric acid, and make the solution ammoniacal and then barely acid with acetic acid. Dilute to 300 ml, heat nearly to boiling, and treat with 20 ml of a 1 per cent alcoholic solution of dimethylglyoxime.[2] Finally make slightly ammoniacal, adding enough ammonia so that the solution barely smells of this reagent. Allow the solution to stand in a warm place for 15 minutes and then cool for half an hour or longer. Finally filter the solution through a Gooch or Munroe crucible, wash thoroughly with hot water, dry at 105° for 90 minutes, and weigh as $Ni(C_4H_7N_2O_2)_2$. To the filtrate add 5 ml more of dimethylglyoxime reagent and make sure that the solution is barely alkaline. There should be no further precipitation.

By this method the nickel in a sample of steel can be determined within about 2 hours. The results are accurate, but lower than those sometimes obtained in practice when the cobalt is determined with the nickel. The precipitate is too voluminous to handle easily when the solution contains more than 0.1 g of nickel.

The above procedure has been found to give excellent results with students over a period of about 25 years. The sample analyzed should not contain more than about 0.04 g of nickel. Good results, however, have been obtained with nearly pure nickel when the HCl solution of 0 15 g of the metal was diluted to a definite volume, the solution mixed, and an aliquot of one-fifth taken for the precipitation.

In nearly every set of directions given since 1907, emphasis is placed on avoiding excess of the reagent because of the solubility of the precipitate in alcohol. As a matter of fact, however, the principal difficulty caused by the use of too much reagent is the precipitation of white needles of dimethylglyoxime itself; the reagent

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[1] O. Brunck, *Stahl und Eisen*, 28, 331.

[2] The volume of the alcoholic solution should never be more than half that of the nickel solution, as the precipitate is slightly soluble in alcohol. About 0.4 g of the glyoxime should be used for each 0.1 g of nickel. A deep red color in the solution shows that ferrous iron is present.

is much less soluble in water than in alcohol. The deposited crystals of dimethyl-glyoxime can be dissolved by washing with hot, dilute ammonia solution. Washing the precipitate with a *little* hot 50 per cent alcohol has been found to be more efficient, and by this treatment but very little of the nickel precipitate is dissolved.

It has been thought that the electrolytic determination of nickel is more accurate, and some directions call for dissolving the dimethylglyoxime precipitate in acid, destroying the organic matter by adding HNO_3 and evaporating with H_2SO_4, and finally depositing the nickel electrolytically from a strongly ammoniacal solution. A skilful analyst can obtain good results in this way, but for students, direct weighing of the precipitate of nickel dimethylglyoxime is better.

Some chemists prefer to titrate the nickel. Wash the nickel dimethylglyoxime precipitate on a paper filter with 3 portions of cold water, dissolve it in 6 N HNO_3, and wash the filter with hot water. Boil the solution 2 minutes, cool, add 5 ml of a solution containing 1 g citric acid, 1.35 g $(NH_4)_2SO_4$ and 1 ml of concentrated ammonia. Neutralize and titrate as described in Chapter XVII.

Removal of Ferric Chloride by Ether.   Method of Rothe[1]

The fact that ferric chloride dissolved in hydrochloric acid, d 1.1, is more soluble in ether than in this acid, is often taken advantage of in the determination of metals such as nickel, manganese, cobalt, copper, aluminum, titanium, vanadium, and chromium in samples of steel. It has also been used for the determination of sulfur in steel after oxidation to sulfuric acid, which does not dissolve in the ether. The underlying principle is the same as that governing the distribution of iodine between water and carbon disulfide (see Vol. I). An example of such a process is the determination of titanium by the method of Barneby and Isham (p. 178). Beryllium chloride and molybdic acid follow the ferric chloride and dissolve in the ether.

The Use of Tannin in Quantitative Analysis

General Principles. The name *tannin* has been given to a widely disseminated group of organic substances that are capable of converting raw animal hides into leather. Common tannin, or gallotannic acid, $C_{14}H_{10}O_9, 2H_2O$, is obtained from gall nuts. It has an astringent taste and the character of a weak acid. Its aqueous solution is really a colloidal suspension of negatively charged particles and will form precipitates, or gels, with positively charged suspensions of certain inorganic compounds by reciprocal flocculation (see Vol. I). The resulting adsorption complexes are voluminous and characteristic precipitates which filter well; upon ignition they yield oxide of a metal in a weighable form.

Tannin as a reagent in quantitative analysis was recommended by Powell and Schoeller for separating tantalum from columbium,[2] and the use of this reagent was extended by them and their collaborators to the determination of other ele-

[1] *Z. anal. Chem.*, 1901, 809.
[2] *Analyst*, 50, 485 (1925).

ments (Ti, Zr, Th, Al, U, and W).[1] Subsequently Moser and his students studied the use of tannin in the analytical chemistry of beryllium and of gallium.[2]

The importance of tannin as a precipitant for aluminum, zirconium, hafnium, thorium, uranium, titanium, columbium, and tantalum is due to the following facts. (1) Under proper conditions the precipitates can be formed from tartrate solutions, which is not the case with respect to the precipitation of the hydroxides by ammonia (cf. p. 168). Tannin is a general precipitant for the above elements (formerly called *earths*) just as hydrogen sulfide is for the heavy metals. (2) In an oxalate solution, a separation into two classes can be made just as with ammonium polysulfide in the analysis of sulfides   Here also one of the groups represents oxides which are acid in nature (Ta_2O_5, Cb_2O_5, TiO_2), and the other group oxides which are more basic (ZrO_2, HfO_2, ThO_2, Al_2O_3, BeO, UO_3, Cr_2O_3, etc.). (3) The colored tannin precipitates are characteristic just as are the colored sulfides. (4) With the aid of tannin, excellent separations can be made of (a) tantalum from columbium in all proportions and (b) small quantities of tantalum and columbium from larger quantities of titanium.

Reagent. Use a freshly prepared 2 to 5 per cent solution of high-grade, commercial gallotannic acid (tannin) in boiling-hot distilled water. The tannin should be practically ash-free. It is also called digallic acid.

The following eight procedures illustrate the use of tannin in quantitative analysis.

1. Precipitation of Aluminum, Zirconium, Thorium, Uranium, Titanium, Columbium, and Tantalum from Tartrate Solution[3]

Fuse 0.25 g or less of the oxides in a silica crucible with 3 to 4 g of potassium bisulfate (cf. p. 174). Dissolve the cold, fused mass in a strong solution containing 3 g of tartaric acid. Repeat the fusion if necessary. Into 200 ml of the acid tartrate solution thus obtained, introduce hydrogen sulfide and add 10 g of NH_4Cl and 10 g of ammonium acetate. Allow the solution to stand for some time in a warm place after saturating with hydrogen sulfide, to allow iron sulfide to flocculate. Filter, wash the precipitate with water containing a little ammonium sulfide and chloride. Boil the filtrate to decompose the ammonium sulfide present and add acetic acid dropwise until the 300 to 500 ml of solution is faintly acid. Heat to boiling, and while boiling introduce tannin solution (1 to 3 g of tannin). Keep the solution on a covered water bath for an hour and filter, with the aid of gentle suction, through an 11-cm washed filter supported on a filtering cone. Before the precipitate becomes compressed and furrowed by suction, rinse it back to the original beaker with a liberal stream of wash liquor (2 per cent NH_4Cl solution containing a little tannin). Churn up the precipitate with some ashless filter pulp (p. 151), return to the filter, wash thor-

[1] *Ibid.*, **52**, 504 (1927); **54**, 709 (1929); **57**, 550 (1932); **58**, 143 (1933).

[2] *Monatsh.*, **48**, 113, 673 (1927); **50**, 181 (1928); **51**, 181, 325 (1929).

[3] Schoeller and Webb, *Analyst*, **54**, 709 (1929).

oughly with the wash liquor, and use a rubber policeman and a little paper pulp to remove the last traces of precipitate from the walls of the beaker.

If the precipitate is not very bulky, the use of suction is unnecessary.

Dry the washed precipitate in a crucible placed on an asbestos mat until the paper is well charred (cf. p. 40), and then ignite with the crucible on a triangle. Cool the crucible, cover with a watch glass, and half fill it with 0.5 N HCl. Heat half an hour on the steam bath, make the resulting solution alkaline to methyl red by adding ammonia, filter, wash with 2 per cent ammonium nitrate solution, and ignite to constant weight of oxides.

The leaching of the precipitate after the first ignition insures the complete removal of alkali salts and of sulfate; this is difficult to effect with bulky precipitates.

The filtrate from the tannin precipitate should be tested for complete precipitation as follows: Heat to boiling, treat with 0.5 g of tannin, and make feebly ammoniacal. This causes the formation of a discolored precipitate, which should be soluble on slight re-acidification, leaving only small dark flocks of organic matter. If not, the additional precipitate must be collected, washed, and added to the main precipitate.

The tannin complexes of Al, Zr, and Th are colorless; those of Ti and Cb, red; those of W and U, brown; and the Ta precipitate, yellow. Ferric salts give a precipitate of an intense purplish black color. The above procedure provides for the removal of iron as sulfide. Tungsten interferes because, although it is not precipitated alone by tannin from tartrate or oxalate solutions, it is adsorbed to a considerable extent by the other precipitates.

2. Separation of Iron from Aluminum[1]

The above method is a reliable and convenient means for separating iron from less than 0.05 g of alumina. The alumina-tannin complex is too bulky to handle when larger quantities of alumina are present, and in such cases an aliquot part of the solution should be taken. The weight of tannin used should be at least 20 times that of the Al_2O_3 obtained by igniting the tannin precipitate; at least 0.5 g of tannin should always be used.

3. Separation of the Acid Tannin Group (TiO_2, Ta_2O_5, Cb_2O_5) from the Basic Tannin Group (Al_2O_3, ZrO_2, ThO_2, UO_2, BeO)[2]

Principle. The members of the "acid tannin group" are precipitated as tannin complexes in a feebly acid oxalate solution which is half-saturated with ammonium chloride; the members of the basic tannin group are not precipitated unless

[1] Schoeller and Webb, loc. cit.
[2] Schoeller and Powell, Analyst, 57, 550 (1932).

ammonia is added. The process gives a clean-cut separation of any one or all of the members of one group from one or more members of the other.

Procedure. Fuse the mixed oxides (up to 0 25 g) with potassium acid sulfate as in the first procedure. Dissolve the cold, fused mass in 75 to 100 ml of saturated ammonium oxalate solution. To the boiling solution add N NH$_4$OH until a faint cloudiness forms, and at once dissolve this in as little HCl as possible; the solution should now be acid to litmus. Add an equal volume of saturated NH$_4$Cl solution and continue boiling while introducing dropwise a fresh 4 per cent solution of tannin. The quantity of tannin used should be 10 to 12 times the weight of "acid oxides" present.

Allow the tannin precipitate to stand on a hot plate for an hour before filtering. Filter the precipitate as directed on p. 222 in Method 1, but this time use as wash liquor a solution containing 5 per cent NH$_4$Cl and 1 per cent (NH$_4$)$_2$C$_2$O$_4$. Ignite the washed precipitate in a tared porcelain crucible.

Always test the filtrate for complete precipitation as follows: Heat to boiling, neutralize with N NH$_4$OH, and treat with tannin dropwise until a slight precipitate is formed. If this is greyish or brownish gray, and soluble on slight acidification, the precipitation of the "acid group" is complete; if yellow or pale orange in color, some of the "acid group" remains. In this case, add tannin under the conditions given above and add the new precipitate to that previously obtained.

To test the weighed precipitate of "acid oxides" for members of the "basic" group, repeat the entire procedure using the same quantity of tannin es in the first case The weight of the new precipitate should be substantially the same as that obtained in the first piece. Leach these oxides with 0.5 N HCl and continue as in Method 1, finally obtaining a weight of purified oxides.

Then, to determine oxides of the "basic" group, take the combined filtrates from the tannin precipitations, add more tannin to the boiling solution and a moderate excess of ammonia. Filter off the tannin precipitate, wash it with 2 per cent NH$_4$Cl solution, and ignite to constant weight of oxides. This weight is usually somewhat high owing to a little SiO$_2$ from the vessels used in the analysis or from the reagents. To correct for this, fuse with KHSO$_4$, dissolve the melt in 0.5 N H$_2$SO$_4$, filter off the insoluble residue, ignite, and call it SiO$_2$. Make a corresponding reduction from the weight of the "basic" oxides.

4. Separation of Tantalum from Columbium[1]

Principle. Tantalum and columbium are precipitated completely from an oxalate solution on adding an excess of tannin solution and neutralizing with ammonia (see section 3); by properly regulating the quantities of reagents, it is possible to accomplish a quantitative separation of these two elements Tantalum requires less tannin than columbium does and the precipitate forms in a more acid solution. The tantalum complex is yellow and the columbium complex is red; coprecipitation of the columbium with tantalum is indicated by the orange-yellow to orange-red color of the tannin precipitate. The progress of the precipitation, therefore, can be controlled by watching the color of the precipitate. It is impossible, however, to effect a quantitative separation by means of a single precipitation if less tantalum than columbium is present.

[1] Schoeller, *Analyst*, **57**, 750 (1932).

Schoeller has devised a scheme of analysis which furnishes (1) a yellow tannin precipitate containing tantalum and no columbium, (2) an orange to red precipitate containing both tantalum and columbium, and (3) a filtrate containing columbium and no tantalum. A complete separation is accomplished by systematic retreatment of the orange to red precipitate whereby three fractions are obtained again, the middle fraction is fractionated, and the process repeated until finally all the tantalum is obtained in the form of a yellow tannin precipitate. The actual working out of the method involves directions which are too lengthy to be given here; the original paper should be consulted for details.

5. Separation of Small Quantities of Tantalum and Columbium from Titanium[1]

Principle. Titanium oxide is amphoteric and forms a sulfate, whereas the earth acids, Ta_2O_5 and Cb_2O_5, do not. A solution of tannin in dilute sulfuric acid, placed in contact with the product formed by fusing TiO_2, Ta_2O_5, and Cb_2O_5 with $KHSO_4$, dissolves $Ti(SO_4)_2$, leaving behind the Ta_2O_5 and Cb_2O_5. If tannin is not present, all three oxides dissolve in the sulfuric acid.

Procedure. Fuse 0.1 to 0.25 g of the mixed oxides with 2 to 3 g of $KHSO_4$ in a silica crucible and make the melt solidify around the sides of the crucible. Pour some of the hot reagent (1 per cent tannin in 1.8 N H_2SO_4) into the crucible and heat gently until the melt becomes detached. Transfer the contents of the crucible to a small beaker, rinse out the crucible with more of the hot reagent, heat the liquid just to boiling, and then, without further heating, allow the mixture to stand for some hours or over night. Filter, wash the residue with 0.5 N H_2SO_4 containing a little tannin, ignite, and weigh the residual Ta_2O_5 and Cb_2O_5.[2]

If the weighed oxides are again fused with a small amount of $KHSO_4$ and the melt dissolved in a little tartaric acid solution, then on boiling with one-quarter the liquid's volume of concentrated sulfuric acid, a characteristic white precipitate of earth acids will be obtained (cf. Vol. I)

The above process is very simple and rapid but not suitable for the separation of large quantities of earth acids from titania. In such cases recourse must be had to the oxalate-salicylate method.[3] In principle, this method consists in dissolving the bisulfate melt of the mixed oxides in ammonium oxalate solution and adding an excess of sodium salicylate, whereby the titanium is converted into soluble, orange-colored sodium titanylsalicylate. The solution is then precipitated with excess of calcium chloride, the precipitated calcium oxalate carrying down the insoluble salicylic complexes of the earth acids

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[1] Schoeller, *Analyst*, **54**, 453 (1934).

[2] If the proportion of titania in the mixed oxides is very high, the pentoxides should be retreated.

[3] Schoeller and Jahn, *Analyst*, **57**, 72 (1932).

6. Determination of Small Quantities of Tungstic Acid[1]

Principle. When a dilute solution of sodium tungstate containing sodium or ammonium chloride is treated with tannin, and acidified, the tungstic acid is precipitated as the brown tannin complex. A small part of the tungsten complex remains in colloidal suspension. Addition of the salt of an alkaloid such as cinchonine produces a flocculent cinchonine tannin complex which acts as a collector of the colloidal tungsten precipitate.

This method replaces the mercurous nitrate precipitation process; it solves the problem of the recovery of small quantities of tungstic acid from solution. It is also to be preferred to the cinchonine precipitation method, which gives low results in the presence of much alkali salt.

Procedure. To 100–150 ml of slightly alkaline solution, such as is obtained after fusing with Na_2CO_3 and extracting with water, add dilute HCl until neutral to phenolphthalein and a fresh solution of 0.5 g tannin in a little water. Part of the tannin will form a white turbidity if much chloride is present. Now make acid to litmus paper, which will cause the brown WO_3 and tannin complex to appear. After a few minutes, heat to gentle boiling and add 10 ml of 2.5 per cent cinchonine solution. Boil 5 minutes longer, and let stand 6 hours or over night. Filter with the aid of filter-paper pulp and wash with a cold 5 per cent NH_4Cl solution containing a little tannin. Pay no attention to a white turbidity that may form in the filtrate. Ignite in a tared porcelain crucible, and weigh the residual WO_3.

7. Beryllium

Beryllium belongs to a third tannin group, the members of which (Be, Mn, Ce, and Y) furnish tannin complexes precipitated in the presence of an excess of ammonia, and soluble in dilute acetic acid[2]

Moser and List[3] base a separation of beryllium from a number of metals of Group III upon the solubility of its tannin complex in acetic acid. The solution is treated with hydrogen sulfide for the removal of heavy metals, and the filtrate is boiled with addition of bromine for the oxidation of ferrous iron. After neutralization with sodium carbonate, the solution is hydrolyzed in the presence of ammonium nitrite and methyl alcohol (p. 150). The precipitate, which contains beryllia and sesquioxides and dioxides of Group III, is dissolved in nitric acid. The solution is neutralized with ammonia, treated with ammonium acetate and nitrate, and acidified with acetic acid. Addition of tannin to the boiling solution precipitates Al, Cr, Fe, Ga, Ti, Zr, and V. Beryllium passes into the filtrate, from which it is recovered by tannin and an excess of ammonia.

[1] Schoeller and Jahn, *ibid.*, **52**, 504 (1927).

[2] Schoeller and Webb, *ibid.*, **59**, 669 (1934).

[3] *Monatsh.*, **51**, 181 (1929).

8. Gallium

Moser and Brukl[1] found tannin to be the best and most sensitive precipitant for gallium. The boiling, weakly acid acetate solution containing 2 per cent of ammonium nitrate is treated drop by drop with 10 per cent tannin solution while stirring. At least 0.5 g of tannin should be added. The bulky precipitate is washed with hot water containing a little ammonium nitrate and acetic acid, and ignited to Ga_2O_3. The procedure separates gallium from zinc, which is of practical importance because gallium occurs in zinc ores. The separation of gallium from aluminum is effected with cupferron.[2]

TUNGSTEN, W.   At. Wt. 183.92

Tungsten is determined as its trioxide, WO_3.

If the tungsten is present as ammonium tungstate, as mercurous tungstate, or as tungstic acid, it can be changed by ignition in the air to yellow tungsten trioxide. Care should be taken not to heat strongly or some of the tungstic acid will be lost by volatilization. The crucible should be uncovered, and the full heat of the burner should not be used. When ignited over a Méker burner in a covered platinum crucible, a slow volatilization of tungstic acid takes place. There is danger of some tungsten being reduced by ignition of ammonium tungstate.

If the tungsten is present as alkali tungstate, the tungstic acid may be precipitated as such, or by means of mercurous nitrate as mercurous tungstate;[3] by ignition the yellow trioxide is obtained and weighed.

The most satisfactory way to determine tungsten is to weigh it as WO_3 after it has separated out as tungstic acid by digestion with HCl or HNO_3, finally in the presence of cinchonine. Precipitation as Hg_2WO_4 followed by ignition to WO_3 is quantitative but other acids such as vanadic, chromic, and molybdic acids also form insoluble mercurous salts under similar conditions so that precipitation with $HgNO_3$ serves best as a group separation.

Precipitation of Tungstic Acid

Moisten the sample with 20 ml of concentrated hydrochloric acid, add 10 ml of concentrated nitric acid, and evaporate carefully to 10 or 15 ml. Rinse down the cover glass and sides of the container with water and dilute to about 150 ml. Add 5 ml of cinchonine hydrochloride solution (prepared by dissolving 12.5 g of cinchonine in 100 ml of 6 N acid) and heat on the hot plate for 30 minutes or longer, stirring occasionally and keeping the temperature just below boiling.

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[1] *Monatsh*, 60, 181 (1928).

[2] *Ibid*, 51, 325 (1929).

[3] See p 226 for a method using tannin and cinchonine hydrochloride.

Allow the tungstic acid to settle and then decant the solution through a filter containing some pulp made by digesting ashless filter paper with acid. Wash the precipitate 3 times with the above cinchonine hydrochloride solution diluted 100-fold. Transfer the precipitate to the filter and continue washing till free from alkali salt. Ignite at a low temperature in an open crucible and weigh the residual WO_3.

Remarks. It is difficult to precipitate tungstic acid by simple evaporation with acid. Sodium tungstate, Na_4WO_4, unites to some extent with free tungstic acid to form an acid tungstate, $Na_2W_4O_{13}$, and this is not easily decomposed by acids. By heating with ammonium hydroxide the acid tungstate can be converted back to normal tungstate, but on adding acid some more of the acid tungstate is likely to form.

Cinchonine hydrochloride prevents the formation both of the acid tungstate and of colloidal solutions upon washing. During the ignition all the organic material is consumed so that the presence of cinchonine in the precipitate does no harm.

Tungstic acid is slowly volatilized by heating at a high temperature. The filter should be consumed at as low a temperature as possible and the heating stopped when the carbon is all gone.

Precipitation of Tungsten as Benzidine Tungstate[1]

If a neutral solution of sodium tungstate is treated with benzidine hydrochloride, a white flocculent precipitate of benzidine tungstate is formed and the precipitate is insoluble in water containing benzidine hydrochloride; when formed in the cold it is hard to filter and, on being washed with pure water, tends to run through the filter. If the precipitate is formed from a hot solution, however, it comes down in a more compact condition and after cooling[2] can be easily filtered and washed without loss with water containing benzidine hydrochloride. The moist precipitate on being heated to 800° yields a residue of WO_3.

The precipitation can also take place satisfactorily from a cold solution if, before adding the precipitant, a little dilute sulfuric acid or alkali sulfate is added to the solution. In this case a mixture of crystalline benzidine sulfate and amorphous benzidine tungstate is formed which can be filtered after standing 5 minutes. The benzidine sulfate is entirely volatile, so that equally good results are obtained by either of the above two procedures.

If the tungsten is present as tungstate after fusing with sodium carbonate, dissolve the melt in water, add a little methyl orange to the clear solution, then hydrochloric acid until the pink color is obtained, and

[1] G. v. Knorre, Ber., 38, 783 (1905)

[2] Since benzidine tungstate is appreciably soluble in hot water containing benzidine hydrochloride, it is always necessary to postpone the filtration until the solution is cold

finally 10 ml of 0.1 N sulfuric acid. Benzidine hydrochloride gives a precipitate which can be filtered in 5 minutes. Wash with dilute benzidine hydrochloride until the evaporation of a few drops of the filtrate on platinum foil leaves no weighable residue. Ignite the moist precipitate as described above.

Preparation of the Benzidine Solution

Triturate 20 g of commercial benzidine in a mortar with water, wash into a beaker with about 400 ml of water, treat with 25 ml hydrochloric acid (d 1.2), and heat until solution is complete and a brown liquid is formed. Filter and dilute to 1 l. Of this solution, 5.6 ml is sufficient to precipitate 0.1 g of WO_3.

If the analysis is carried out in the presence of sulfuric acid, it is necessary to add at least 1 ml of the benzidine solution for 10 ml of 0.1 N sulfuric acid added.

Preparation of the Wash Liquid

Dilute 10 ml of the above solution with distilled water to a volume of 300 ml.

Determination of Tungsten in Steel

Modern alloy steels often contain from 0.5 to 20 per cent of tungsten. It may be present as WC or as Fe_3W. In mild steel, tungsten up to 1 per cent has little effect upon the mechanical properties, but "high-speed" steels containing 13–18 per cent tungsten, 2.5–5 per cent chromium, 0.6–0.7 per cent carbon, and up to 1 per cent vanadium are characterized by their ability to be worked at a speed 3 to 5 times as great as that at which plain carbon steels can be worked, and these high-speed steels retain their hardness even at a red heat. The steel can be hardened at a white heat which would ruin a plain carbon steel. Probably double carbides of Cr and W are formed in the steel and remain in it on rapid cooling and to some extent on slow cooling.

After thorough oxidation of a sample of steel by treatment with acid and an oxidizing agent, the tungsten is obtained as a hydration product of yellow WO_3 (tungstic acid anhydride). This, like silicic acid, is insoluble in water but tends to form colloidal solutions. The problem, therefore, is to oxidize the tungsten to tungstic acid and then to make sure that it is all precipitated together with any silicic acid that may be present. The complete precipitation is aided by adding some cinchonine hydrochloride to the solution; cinchonine is an alkaloid, or weakly basic organic substance of complicated composition. In the following

rapid method, the precipitation of the tungstic acid is not quite complete, but this deficiency is compensated by the presence of small quantities of impurities.

Procedure. Treat 1.0 g of the steel in a 400-ml beaker with 50 ml of concentrated HCl, and heat in the covered beaker until all the metal is decomposed. Remove from the heat and add cautiously 5 to 7 ml of concentrated HNO_3. Cover the beaker, and boil for 5 minutes to oxidize all the iron and convert the tungsten to yellow tungstic acid. Remove from the heat, wash the under part of the watch glass and the sides of the beaker with hot water, dilute to 75–100 ml, and filter through a 9-cm ashless filter containing some filter-paper pulp made from ashless filters. Wash the precipitate alternately, three times each, with 10-ml portions of hot 6 N HCl and hot water, and finally with four similar portions of hot water. Transfer the paper and precipitate to a weighed platinum crucible, ignite, and weigh. Treat the impure WO_3 with sulfuric and hydrofluoric acids (see Chapter XII) to volatilize SiF_4, and call the residue WO_3.

Determination of Tungsten in Ores[1]

Procedure. Weigh out accurately about 1 g of the finely ground ore into a 400-ml beaker. Moisten the sample with 5 ml of water, and add 100 ml of concentrated hydrochloric acid. Cover the beaker and digest at about 60° for at least an hour. Stir from time to time to prevent the formation of any crust. Then evaporate slowly to about 50 ml. Add 40 ml more of strong hydrochloric acid and 20 ml of concentrated nitric acid, and evaporate to about 10 ml. During these operations, especially when fresh acid is added, stir the material at the bottom of the beaker so that it does not become encrusted.

Rinse down the cover glass and the sides of the beaker and dilute with water to about 150 ml. If, by accident, the solution was evaporated to dryness during the above treatment, add 20 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid to the residue and evaporate to 10 or 15 ml.

To the diluted solution add 5 ml of cinchonine hydrochloride solution (12.5 g of cinchonine dissolved in 100 ml of 6 N hydrochloric acid) and heat on the hot plate for 30 minutes or longer. The solution should be at a temperature just below the boiling point and should be stirred occasionally.

Allow the tungstic acid anhydride to settle and then decant the solu-

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[1] Recommended by J. A. Holladay and found satisfactory by collaborative work in 17 different laboratories under the direction of W. F. Hillebrand.

tion through a filter which contains some pulp made by digesting asbless filter paper with acid. Wash the precipitate three times with a solution containing 10 ml of the above cinchonine solution to a liter of hot water. Then transfer the precipitate to the filter and wash with this same diluted cinchonine solution.

Wash the tungstic anhydride back into the original beaker by a jet of water, using about 25 ml to accomplish this. Add 6 ml of concentrated ammonia solution and heat gently, with the beaker covered, for about 10 minutes to convert all the tungstic acid into ammonium tungstate. Rinse down the sides of the beaker with hot, dilute ammoniacal ammonium chloride solution (200 ml of concentrated ammonia, 800 ml of water, and 10 ml of concentrated hydrochloric acid). Stir up the contents of the beaker and filter through the same filter that was used for the previous filtration. Collect the filtrate in a 400-ml beaker and wash the original beaker and filter with the hot ammoniacal solution. The presence of a little ammonium chloride in this ammoniacal solution prevents colloidal silicic acid from passing into the filtrate.

The residue on the filter is usually free from tungsten, but it should be tested (see below). Ammonium and sodium salts tend to prevent the complete precipitation of tungstic acid, so that it is important, next, to remove the excess ammonia. After this has been evaporated off, add 20 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid and evaporate to about 15 ml. Dilute with 150 ml of water and precipitate the remainder of the tungstic acid by treatment with cinchonine solution as described above.

After filtering and washing the precipitate as before, ignite it carefully in a weighed platinum crucible. The presence of the paper pulp causes the precipitate to form a porous, friable mass and makes it easy to oxidize the carbon. If the ignition is made in a muffle, the introduction of oxygen is advantageous. After burning off the carbon, at as low a temperature as possible, weigh the precipitate and correct for silica by the usual treatment with hydrofluoric acid.

If the tungstic acid is heated over the full flame of the burner, some of it will be lost by volatilization. After the removal of the silica, the residue should be heated to dull redness for only 1 minute. Heated in the muffle, the maximum temperature should not exceed 800°. The ignited tungsten trioxide, WO_3, should have a clean, lemon-yellow color.

To test for tungsten the residue that is insoluble in ammonia, ignite it in an iron crucible and fuse the ash with a small quantity of sodium peroxide mixed with a little sodium carbonate. Reducible metals are likely to ruin a platinum crucible if the residue and filter paper are heated in it. Extract the melt with water and filter. Acidify the aqueous

extract with hydrochloric acid, add 5 ml of cinchonine hydrochloride solution, and heat for several hours to see if any yellow tungstic acid anhydride is formed.

Rapid Method for Determining Tungsten in Ores

Treat 1 g of ore in a platinum dish with about 10 ml of HF, 25 ml of concentrated HCl, and 10 ml of $9 N$ $HClO_4$. Heat carefully until the sample is decomposed, adding more HF if necessary. Evaporate on an air bath to fumes of $HClO_4$. Dilute with water and transfer to a 400-ml beaker. The WO_3 can usually be removed from the dish by rubbing with a rubber policeman. If any stain adheres, dissolve it in a little concentrated ammonia and add to the acid solution. Add 75 ml of concentrated HCl and 25 ml of concentrated HNO_3, and evaporate to about 20 ml at a temperature a little below the boiling point. Dilute with 100 ml of cold water, add 10 ml of cinchonine reagent (p. 230), and allow 2 hours for the precipitate to settle.[1] Filter, and wash with dilute cinchonine solution as described on p. 231. Ignite the residue in a weighed platinum crucible to a dull red heat and weigh. Treat with HF and H_2SO_4 as described on p. 230 to make sure that the original treatment removed all SiO_2.

Separation of Molybdenum from Tungsten

(a) The Sulfuric Acid Method

This method, proposed by M. Ruegenberg and E. F. Smith,[2] depends upon the fact that unignited molybdic acid is readily dissolved by heating with sulfuric acid (d 1.38), while tungstic acid is not.

W. Hommel[3] tested this method in the author's laboratory, and could not obtain good results except by digesting the moist oxides with *concentrated* sulfuric acid, and afterward diluting with three times as much water.

Procedure. α. *Both Acids Are Present in a Moist, Freshly Precipitated State.* Cover the mixture with concentrated sulfuric acid in a porcelain dish and heat over a free flame. By this means, usually a small amount of the tungstic acid is oxidized to the blue oxide, so that the yellow pre-

[1] The above procedure is essentially that recommended by Ledoux and given in *Bull.* 212 of the Bureau of Mines. Ledoux recommends fusing the final WO_3 precipitate with sodium carbonate, leaching with water, filtering, igniting, and weighing the insoluble residue to correct for impurities in the WO_3 precipitate.

[2] *J. Am. Chem. Soc.*, 22, 772.

[3] Inaug. Dissert., Giessen, 1902.

cipitate of tungstic acid is tinted with green. On adding one or two drops of dilute nitric acid, the green color disappears and the tungstic acid is of a pure yellow color. After digesting for half an hour, the separation is complete. Cool, dilute the liquid with three times its volume of water, filter, wash with water containing sulfuric acid, then two or three times with alcohol, ignite (after burning the filter by itself) in a porcelain crucible, and weigh as WO_3.

Precipitate the molybdenum in the filtrate by passing hydrogen sulfide into the sulfuric acid solution in a pressure flask, and treat the precipitate as described on p. 114.

If only a little sulfuric acid is used for the separation, the filtrate from the tungstic acid can be evaporated in a platinum dish, the sulfuric acid driven off for the most part, and the residue washed into a weighed platinum crucible with ammonia, and then evaporated, ignited, and weighed. If large amounts of molybdenum are present, however, it is always safer to precipitate the molybdenum as sulfide.

β. Tungsten and Molybdenum Are Present in the Form of Their Ignited Oxides. These ignited oxides cannot be separated by treatment with sulfuric acid. According to W.-Hommel, they can readily be brought into solution by heating for half an hour on the water bath with concentrated ammonia in a pressure flask, shaking frequently.

After cooling, wash the contents of the flask, whether dissolved or not, into a porcelain dish, evaporate to dryness, and treat as described under (α).

It is still better to fuse the ignited oxides with four times as much sodium carbonate, and treat the melt as described under (α).

(b) Sublimation Method[1]

If a mixture of the trioxides of tungsten and molybdenum, or of their alkali salts, is heated at 250–270° in a current of dry hydrochloric acid, the molybdenum is volatilized completely as $MoO_2 \cdot 2HCl$, which collects on the cooler parts of the tube as a beautiful, white, wool-like sublimate, while the tungsten trioxide remains behind in the boat.

Procedure. Weigh out about 0.3 g of the oxides of the two elements, or their sodium salts, into a porcelain boat, and place the boat in a tube made of difficultly fusible glass, of which one end is bent vertically downward and is connected with a Péligot tube containing a little water. Insert the horizontal arm of the tube through a heated air bath, and connect with an apparatus for generating hydrogen chloride gas. Pass this gas through a flask containing concentrated hydrochloric acid, and

[1] Péchard, *Compt rend*, 114, 173, and 46, 1101.

then through concentrated sulfuric acid. As soon as the temperature has reached about 200° the sublimation of the molybdenum begins. From time to time drive over the sublimate that collects in the combustion tube toward the Péligot tube[1] by carefully heating with a free flame, to see whether any more molybdenum is being volatilized. After heating for 1.5-2 hours, the operation is usually complete. Remove the boat containing tungsten trioxide alone or with sodium chloride. If only the tungsten trioxide is present, weigh after drying in a desiccator over caustic potash; if, however, sodium chloride is present (when the tungsten was originally present as sodium tungstate), remove this by treatment with water, and weigh the filtered WO_3 after ignition.

For the determination of the molybdenum, wash out the sublimate in the tube by means of water containing a little nitric acid, and carefully evaporate the nitric acid solution of the entire sublimate to dryness in a porcelain dish. Dissolve the residue in ammonia, wash into a porcelain crucible, evaporate to dryness, and change to MoO_3 by gentle ignition.

(c) The Tartaric Acid Method of H. Rose

To the aqueous solution of the alkali salts of the two metals add considerable tartaric acid and an excess of sulfuric acid. Precipitate the molybdenum according to p. 114, by hydrogen sulfide in a pressure flask. Filter off the molybdenum sulfide and change by roasting in the air to the trioxide. For the determination of the tungsten, destroy the tartaric acid by repeated evaporation with nitric acid, filter off the precipitated tungstic acid, and change by ignition to the trioxide.

Remark. This method gives correct results, but is not so satisfactory as the preceding one on account of the time consumed in removing the tartaric acid.

Analysis of Tungsten Bronzes

The analysis of these alkali salts of complex tungsten acids, discovered by Wöhler in 1824,[2] offered considerable difficulty for a long time because acids do not decompose them very readily.

By fusion with alkalies in the air, or better still in the presence of potassium nitrate, the tungsten bronzes can be converted without difficulty into normal alkali tungstate, and the tungsten determined by one of the methods already described.

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[1] By the absorption of the $MoO_3 \cdot 2HCl$ in the water of the Péligot tube, the brick-red acid chloride, $Mo_3O_8Cl_2$, is often formed:

$$3[MoO_3 \cdot 2HCl] + 2HCl = 4H_2O + Mo_3O_8Cl_2$$

This substance is insoluble in hydrochloric acid, but readily soluble in nitric acid.

[2] Pogg. Ann., 2, 350.

It is obvious that the alkalies cannot be determined in the same sample, so that Philipp[1] proceeded as follows:

Treat the bronze with ammoniacal silver nitrate solution. The WO_2 is thereby oxidized to WO_3 and an equivalent amount of silver is precipitated, but the whole of the tungsten dissolves as alkali and ammonium tungstates. In the filtrate obtained after filtering off the deposited silver, precipitate the tungstic acid by treatment with nitric acid and determine as WO_3. After removing the excess of silver, by precipitating it as the chloride, evaporate the filtrate to dryness with the addition of sulfuric acid, and weigh the alkali as sulfate.

Although the above method affords satisfactory results in the analysis of bronzes containing comparatively little tungsten, it is wholly inadequate for bronzes rich in tungsten. The method of Brunner,[2] which follows, is applicable in all cases. It is based upon the fact that the bronzes can be transformed very easily, and without loss of alkali, into normal tungstates by heating with ammonium persulfate, or ammonium acid sulfate.

Procedure. Treat 0.5 g of the finely powdered bronze in a porcelain crucible with 2 g of alkali-free ammonium sulfate and 2 ml of concentrated sulfuric acid,[3] heating gently over a small flame. During the heating, frequently move the crucible cautiously to shake its contents about a little. The escape of gases from the crucible soon ceases, and when sulfuric acid vapors begin to be evolved the decomposition of the bronze results.

With sodium and lithium bronzes the fused mass appears greenish, whereas with a potassium bronze the color is yellowish white. After a part of the ammonium sulfate has been volatilized, allow the mass in the crucible to cool; add another gram of ammonium sulfate and 1 ml of concentrated sulfuric acid. Again heat the contents of the crucible as before until sulfuric acid fumes come off thickly; then allow the crucible to cool.

Soften the greenish or yellowish white residue by treating with water and rinsing into a porcelain dish. After adding 50 ml of concentrated nitric acid, digest the contents of the evaporating dish on the water bath for 3 or 4 hours, and then, after diluting with water, filter off the residue of pure yellow tungstic acid.

To recover the small amount of tungstic acid remaining in the filtrate, evaporate as far as possible on the water bath, allow to cool, dilute with a little water, carefully treat with an excess of ammonia, again evaporate on the water bath, and treat as described on p. 227.

Evaporate the final filtrate from the tungstic acid determination to

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[1] *Ber.*, **15**, 500 (1882).

[2] *Inaug. Dissert.*, Zürich, 1903.

[3] If ammonium persulfate is used the addition of sulfuric acid is unnecessary. The only objection to the use of the persulfate is that the commercial salt often contains some potassium persulfate.

dryness, expel ammonium salts by ignition and weigh the residue of alkali sulfate (cf. pp. 270 and 278).

Separation of Tungsten from Tin[1]

Mix 1 g of the finely powdered mineral in an iron crucible with 8 g of sodium peroxide, and carefully fuse the mixture over a Bunsen burner for about 15 minutes. After cooling, soften the melt with water and transfer into a 250-ml flask (if lead is present, conduct carbon dioxide into the solution for a few minutes), dilute the solution to the mark, mix well and filter through a dry filter, rejecting the first few milliliters of the filtrate.

For the determination of the tungstic acid, take 100 ml of the filtrate and proceed as described on p. 227.

For the determination of the tin, use a second 100 ml of the original alkaline solution. Treat with 45 ml of concentrated hydrochloric acid, to precipitate tungstic and stannic acids. Add 2 or 3 g of pure zinc to change the tungstic acid to the blue oxide and reduce the stannic acid to metallic tin. Allow the mixture to stand quietly for an hour at a temperature between 50° and 60°. The tin then goes into solution as stannous chloride, and the greater part of the tungsten remains undissolved in the form of the blue oxide. Filter off the latter, and wash. In this way the whole of the tin should be obtained in an acid solution, in the presence of a small amount of tungsten, which does no harm. Dissolve the blue oxide on the filter, however, in hot, dilute ammonia solution to make sure that it contains no trace of metallic tin. If it does, dissolve the small particle of tin in a little hydrochloric acid and add the resulting solution to the main solution of the tin.

Now dilute the solution with water and precipitate the tin as stannous sulfide by introducing hydrogen sulfide gas. Filter off the precipitate, ignite in a porcelain crucible, and weigh as SnO_2 (see p. 97). Or dissolve the moist precipitate of stannous sulfide in potassium hydroxide solution and determine tin by electrolysis (see p. 97).

According to Donath and Müller[2] a mixture of stannic oxide and tungstic acid may be separated as follows: Ignite the mixture with powdered zinc for 15 minutes in a covered porcelain crucible. After cooling, heat the spongy mass in the crucible in a beaker with 4 N hydrochloric acid (1 : 2) until evolution of hydrogen is no longer perceptible. Allow the solution to cool somewhat and add powdered potassium chlorate little by little until the blue tungsten oxide is completely trans-

[1] Cf. H. Augenot, *Z. angew. Chem.*, **19**, 140 (1906).

[2] *Wiener Monatsh.*, **8**, 647 (1887).

formed to yellow tungstic acid, and the liquid no longer shows any blue tinge. Dilute with $1\frac{1}{2}$ times as much water, and after standing 24 hours filter off the tungstic acid, washing the precipitate first with dilute nitric acid and then with 1 per cent solution of ammonium nitrate. Dry, ignite, and weigh as WO_3. Determine the tin in the filtrate as above.

Separation of Tungstic Acid from Silica

When a mixture of tungstic and silicic acid is at hand, such as is obtained by evaporation with nitric acid, the silicic acid may be removed by treating the ignited residue with hydrofluoric acid and a large excess of sulfuric acid.

VANADIUM, V. At. Wt. 50.95

Vanadium is determined as the pentoxide, V_2O_5. The most convenient method for determining vanadium is a volumetric process; it will be discussed in Chapter XV.

If vanadium is present as ammonium or mercurous vanadate, it can be easily changed to the pentoxide by ignition; the pentoxide is a reddish brown fusible substance which solidifies as a radiating, crystalline mass. If vanadic sulfide is carefully roasted in the air, it is also changed quantitatively to the pentoxide.

In the analysis of most minerals containing vanadium, the vanadium is separated from the other metals present by fusing with a mixture of 6 parts sodium carbonate and 1 part potassium nitrate. After cooling, the melt is extracted with water, whereby the sodium vanadate goes into solution while most of the metals are left behind in the form of oxides or carbonates. If phosphorus, arsenic (molybdenum, tungsten), and chromium are present, these elements also dissolve on treating the melt with water in the form of the sodium salts of the corresponding acids.

In practice, therefore, the vanadium is usually met with as the sodium salt of vanadic acid, and it is a matter of separating it from the aqueous solution obtained after fusing with sodium carbonate and potassium nitrate, and of separating it from the other acids which are likely to accompany it (phosphoric, arsenic, and chromic acids).

Precipitation of Vanadic Acid from a Solution of Sodium Vanadate

The Lead Acetate Method of Roscoe[1]

Principle. If a solution weakly acid with acetic acid is treated with lead acetate, orange-yellow lead vanadate is precipitated quantitatively. The lead vanadate,

[1] *Ann. Chem. Pharm., Suppl.,* 6, 102 (1872).

however, does not possess a constant composition, so that the amount of vanadium present cannot be determined by weighing the precipitate. After being washed, it is dissolved in as little nitric acid as possible, the lead precipitated as lead sulfate, and the vanadium determined in the filtrate by evaporating the filtrate, driving off the excess of sulfuric acid, and weighing the residual V_2O_5.

Procedure. Fuse with sodium carbonate and a little potassium nitrate, cool, extract with water to dissolve the alkali salts, and filter. Nearly neutralize the solution with nitric acid, and stir into it an excess of lead acetate solution; the voluminous precipitate will soon coagulate and settle to the bottom of the beaker leaving a perfectly clear supernatant liquid. The precipitate is at first orange-colored, but on standing it gradually becomes yellow and finally perfectly white. Filter and wash with water containing acetic acid until a little of the filtrate will leave no residue on evaporation. Wash the precipitate into a porcelain dish, dissolve the part remaining on the filter in as little as possible of hot, dilute nitric acid, and add the solution to the main part of the precipitate, to which add enough nitric acid to dissolve it completely. Then add an excess of sulfuric acid, evaporate on the water bath as far as possible, and finally heat over a free flame until dense fumes of sulfuric acid are evolved. After cooling, add 50–100 ml of water, filter off the lead sulfate, and wash with dilute sulfuric acid until 1 ml of the filtrate will show no yellow color with hydrogen peroxide. The lead sulfate should be white and free from vanadium; it will be so, provided that enough sulfuric acid was used and the mass was not heated until absolutely dry before diluting with water. Evaporate the filtrate containing all the vanadic acid in a porcelain dish to a small volume, transfer to a weighed platinum crucible, evaporate further on the water bath, and finally in an air bath until all the sulfuric acid is removed. Ignite the contents of the open crucible for some time[1] at a faint-red heat and finally weigh as V_2O_5.

Remark. Instead of decomposing the lead vanadate by means of sulfuric acid, Holverscheidt recommends precipitating the lead as sulfide by means of hydrogen sulfide and determining the vanadium in the filtrate. For this purpose boil the blue-colored filtrate from the lead sulfide precipitate (which contains some vanadyl salt) to expel the excess of hydrogen sulfide and filter off the deposited sulfur. Add a few drops of nitric acid, evaporate the solution to dryness, and change the reddish yellow hydrate of vanadic acid by gentle ignition into the pentoxide of vanadium.

Lead may also be separated from the vanadic acid as lead chloride. In this case it is necessary to add 15 volumes of alcohol to the solution.

The separation of vanadium as the sulfide by acidifying a solution of an alkali vanadate that has been treated with an excess of ammonium sulfide is not admissible,

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[1] On expelling the sulfuric acid, there are finally formed some green and brown crystals of a compound of vanadic acid with sulfuric acid; these are decomposed only at a faint-red heat.

for only a part of the vanadium is precipitated as the brown sulfide, the rest remaining in solution in the form of vanadyl salt. H. Rose called attention to the inaccuracy of this method, but this has not prevented its being recommended in some works on analytical chemistry.

Separation of Vanadium from Arsenic Acid

Most minerals containing vanadium also contain arsenic, and after extracting the melt, obtained by fusion with sodium carbonate and niter, *with water*, both elements go into solution. For their separation, make the solution acid with dilute sulfuric acid and introduce sulfur dioxide into the hot liquid; the vanadic acid is reduced to vanadyl salt and the arsenic to arsenious acid. After boiling to remove the excess of sulfur dioxide, saturate the solution with hydrogen sulfide and filter off the precipitate of arsenic trisulfide. Remove hydrogen sulfide from the filtrate by boiling, evaporate with nitric acid to form vanadic acid again, make the solution alkaline with sodium carbonate, and determine the vanadium by one of the above methods.

Separation of Vanadium from Phosphoric Acid

If the aqueous solution obtained after the soda-niter fusion contains phosphoric as well as vanadic acid, both are precipitated by mercurous nitrate in a neutral solution. By igniting and weighing the washed precipitate the sum of the $V_2O_5 + P_2O_5$ is obtained. When P_2O_5 is present the V_2O_5 does not melt, but only sinters together. Fuse the ignited oxides with an equal weight of sodium carbonate, dissolve the melt in water, make the solution acid with sulfuric acid, and boil with sulfurous acid to reduce the vanadic acid to vanadyl sulfate, which will be recognized by the pure blue color that the solution assumes. Pass carbon dioxide into the boiling solution until the excess of sulfurous acid is removed, and then allow to cool. To the cold solution, now about 100 ml in volume, add 200 ml of a 75 per cent solution of ammonium nitrate and 50 ml of ammonium molybdate solution (cf. Remark, p. 240). Heat the solution to about 60°, and set aside to stand for 1 hour. Decant the clear liquid through a filter, and wash three times by decantation with 50 ml of the proper wash liquid (see "Phosphoric Acid"). Dissolve the precipitate by pouring 10 ml of 8 per cent ammonia through the filter into the beaker containing the bulk of the precipitate and finally wash the filter with 30 ml of water. To this solution add 20 ml of a 34 per cent ammonium nitrate solution and 1 ml more of ammonium molybdate, heat just to boiling, and reprecipitate the phosphoric acid by the addition of 20 ml of hot 25 per cent nitric acid. Determine the phos-

phoric acid by the method of Woy (see "Phosphoric Acid"). Deduct the amount of P_2O_5 found from the sum of the oxides to get the weight of V_2O_5.

Remark. A. Gressly tested this method in the Zürich laboratory and made the interesting observation that, if about 0.15 g of V_2O_5 was present with 0.1 g P_2O_5, no trace of the latter could be detected according to the procedure of Woy, even on boiling the solution. On the other hand, an immediate precipitation was produced if a stronger solution of ammonium molybdate was used (75 g of ammonium molybdate dissolved in 500 ml of water) and this solution poured into 500 ml of nitric acid, d 1.2.

The above-described separation gives correct results only when the vanadium is present as vanadyl sulfate; if vanadic acid is present it is precipitated with the phosphoric acid. If the solution is allowed to stand after the addition of the ammonium molybdate, the vanadyl sulfate is gradually oxidized to vanadic acid; the precipitate therefore should not be allowed to stand long before filtering.

Separation of Vanadium from Molybdenum

Precipitate the molybdenum as sulfide from sulfuric acid solution by the action of hydrogen sulfide under pressure as described on p. 114. Ignite and weigh as MoO_3.

Boil off hydrogen sulfide from the filtrate and determine vanadium as described under "Separation of Vanadium from Arsenic Acid" on p. 239.

Determination of Vanadium and Chromium in Iron Ores and Rocks

As vanadium often occurs in many ores of iron and in rocks, although in very small amounts, it is often of interest and of importance to be able to determine it under such conditions. For this purpose, W. F. Hillebrand[1] proceeds as follows:

Fuse 5 g of the finely powdered mineral with 20 g sodium carbonate and 3 g potassium nitrate over the blast lamp. Extract the fused mass with water, add a few drops of alcohol to reduce the green manganite, and filter off the residue.[2]

The aqueous solution contains sodium vanadate and often phosphate, chromate, molybdate, aluminate, and considerable silicate as well. First of all, remove the aluminum and the greater part of the silicic acid by nearly neutralizing the alkaline solution with nitric acid.[3] It is very important not to make the solution acid at this point on account

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[1] *U. S. Geol. Survey Bull.*, 700.

[2] If considerable vanadium is present, the insoluble residue may contain vanadium and should be fused with soda and niter again.

[3] Determine the amount of nitric acid necessary to neutralize 20 g of sodium carbonate by a blank test.

of the reducing action of the nitrous acid set free from the nitrite formed during the fusion. Evaporate the nearly neutral solution to approximate dryness, take up in water, and filter.[1]

Treat the cold alkaline solution with an almost neutral solution of mercurous nitrate until no further precipitation takes place. The somewhat voluminous precipitate contains, besides mercurous carbonate, also mercurous chromate, vanadate, molybdate, arsenate, and phosphate, if the corresponding elements are present in the mineral. If the precipitate is too bulky, cautiously add a little nitric acid, and then a drop of mercurous nitrate in order to see whether the precipitation is complete.

Heat the liquid to boiling, filter, wash the precipitate with water containing ammonium nitrate, dry, and ignite in a platinum crucible at as low a temperature as possible. Fuse the ignited residue with a little sodium carbonate, extract the melt with water, and, if yellow-colored, filter into a 25-ml flask and determine the amount of chromium colorimetrically by comparing its color with a carefully prepared solution of potassium chromate.

Then slightly acidify the solution with sulfuric acid, and precipitate the molybdenum, arsenic, and traces of platinum by hydrogen sulfide in a pressure flask. Filter off the precipitated sulfides, carefully ignite the filter together with the precipitate in a porcelain crucible, add a few drops of sulfuric acid, and heat the crucible again until the acid is almost completely removed. On cooling the mass is colored a beautiful blue if molybdenum is present.

Expel hydrogen sulfide from the filtrate by boiling and introducing carbon dioxide at a volume of not over 100 ml. Then titrate the *hot* solution to a pink color with 0.01 N potassium permanganate solution (cf. Chapter XV). To obtain absolutely accurate results, reduce the hot solution again with sulfur dioxide, expel the excess with carbon dioxide, and repeat the titration. This result is usually a trifle lower and should be taken as correct.

$$5V_2O_2(SO_4)_2 + 2KMnO_4 + 22H_2O = 2KHSO_4 + 2MnSO_4 + 10H_3VO_4 + 6H_2SO_4$$
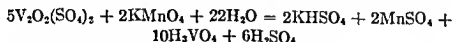
This method gives correct results only when the amount of chromium present is very small, which it usually is.

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[1] The residue of aluminum hydroxide and silicic acid rarely contains vanadium, but often does contain chromium. If it is desired to determine the chromium, evaporate the residue to dryness with hydrofluoric and sulfuric acids, fuse the dry mass with soda and niter again, and add the aqueous solution of the melt to the main solution.

If more than 5 mg of chromium is present a correction must be made, for a measurable amount of permanganate is used up in oxidizing the chromium. This is determined by taking a solution containing the same amount of chromate as the analyzed solution, reducing it with sulfurous acid, and titrating with permanganate. The amount of permanganate now used must be subtracted from the amount used in the analysis, and from the difference the amount of vanadium can be calculated.

Determination of Vanadium and Molybdenum in Steel

Modified Method of A. A. Blair[1]

Dissolve 2 g of the steel in 50 ml 6 N nitric acid, evaporate to dryness, and bake the residue to decompose nitrates. Take up with hydrochloric acid and carry out the Rothe ether separation as described on p. 179. Practically all the molybdenum will be dissolved in the ether, and all the chromium, vanadium, and nickel will be in the aqueous acid solution.

To determine molybdenum, evaporate the ether solution nearly to dryness by carefully heating over warm water, away from any flame. Add 10 ml of sulfuric acid and again evaporate to remove hydrochloric acid. Cool, dilute with 100 ml of water, and reduce the ferric salt by adding ammonium bisulfite. Boil off the excess of sulfurous acid, cool, transfer to a pressure flask, saturate with hydrogen sulfide, and determine molybdenum as MoO_3 according to p. 114.

Take the aqueous acid extract from the ether separation for the determination of vanadium. Remove the dissolved ether by heating on the water bath, add nitric acid in excess, and evaporate to remove hydrochloric acid. When the solution is almost sirupy, add 20 ml of hot water and heat with a few drops of sulfurous acid to reduce any chromic acid that may have been formed, but take care not to reduce the vanadium. Boil and slowly pour the hot solution, while stirring, into an excess of a boiling 10 per cent solution of sodium hydroxide. One milliliter of the alkali will neutralize about 0.4 ml of 6 N nitric acid. Boil a few minutes, allow the precipitate to settle, filter, and wash with hot water till free from alkali. The precipitates contain hydroxides of iron, chromium, nickel, copper, manganese, etc., and the filtrate contains sodium vanadate. To remove traces of chromium, make acid with nitric acid, boil, and again neutralize with hot caustic soda. Make this last filtrate acid with acetic acid, heat to boiling, and precipitate the vanadium with hot lead acetate solution. Filter off the yellow lead

[1] J. Am. Chem. Soc., 30, 1228.

vanadate precipitate, dissolve it in hot dilute hydrochloric acid and, if much lead is present, evaporate the solution nearly to dryness, cover with alcohol, and filter off the lead chloride. Evaporate off the alcohol and titrate the vanadium as in the preceding method.

Usually it is unnecessary to remove the lead. Evaporate the hydrochloric acid solution to dryness, add 50 ml of 12 N hydrochloric acid, and again evaporate nearly to dryness. Add 10 ml of concentrated sulfuric acid and evaporate to fumes. Cool, dilute to 150 ml, heat to 60°, and titrate slowly with permanganate. One milliliter of 0.1 N permanganate reacts with 0.00510 g of vanadium.

Remark. For the routine analysis of vanadium in steel, the American Society for Testing Materials has sanctioned the determination of vanadium without removing chromium. In this case, after the removal of the ether in the above procedure, add 25 ml of concentrated sulfuric acid and evaporate to fumes. Cool, add 25 ml of water and a slight excess of 2.5 per cent permanganate solution. Add 15 ml of concentrated hydrochloric acid, again evaporate to fumes, cool, dilute to 150 ml, and titrate with permanganate at 60°.

Campagne[1] showed that good results can be obtained by reducing the vanadium by evaporation with hydrochloric acid when not more than 0.1 g of vanadium is present. The reduction with sulfurous acid, as in the preceding method, is safer.

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[1] *Compt. rend*, 137, 570 (1903).

CHAPTER IV

GROUP IV OF CATIONS

CALCIUM, STRONTIUM, BARIUM

CALCIUM, Ca.   At. Wt. 40.08

Forms: CaO, $CaC_2O_4 \cdot H_2O$, $CaCO_3$, $CaSO_4$

1. Determination as Calcium Oxide (Lime), CaO

For the determination of calcium as CaO, it is best precipitated as the oxalate and converted to the oxide by strong ignition. The solution should contain no other cation besides magnesium and alkalies. Enough ammonium salt should be present to prevent the precipitation of $Mg(OH)_2$ upon adding ammonium hydroxide.

Procedure. Heat the dilute, slightly acid solution to boiling and add a slight excess of hot ammonium oxalate solution. Slowly neutralize with ammonium hydroxide, while stirring, and allow the precipitate to settle for about 4 hours. Add a little more ammonium oxalate to make sure that the precipitation is complete. Decant off the clear liquid through a filter, cover the precipitate with boiling water containing ammonium oxalate,[1] allow to settle, filter, and repeat this washing by decantation 3 times. Finally transfer the precipitate to the filter and wash with a hot, very dilute solution of ammonium oxalate, until free from chloride. Place the moist filter in a platinum crucible and ignite carefully. Heat the precipitate cautiously at first, so that the too rapid evolution of carbonic oxide will not cause loss. After the filter is burnt and the precipitate is perfectly white, cover the crucible and heat strongly over a Méker burner or blast lamp for 20 minutes.

Allow the crucible to cool to about 100° in the air and then for 15 minutes in a desiccator. Weigh as CaO. Heat for another 10 minutes over the Méker burner to make sure that all the calcium carbonate has been decomposed and again weigh.

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[1] T. W. Richards found that the calcium oxalate precipitate is appreciably soluble in pure water but practically insoluble in a dilute solution of ammonium oxalate (Z. anorg. Chem., 28, 85 (1901)).

During the ignition, the following reactions take place:

$$(1) \quad CaC_2O_4 \rightarrow CaCO_3 + CO \text{ (at dull redness)}$$
$$(2) \quad CaCO_3 \rightarrow CaO + CO_2 \text{ (at about } 1000°)$$

Remarks. With an ordinary Bunsen burner and an open crucible but little calcium oxide is formed. It is difficult to convert the precipitate completely to oxide if a *porcelain* crucible is used but if loss of heat by radiation is partly stopped by covering the *platinum* crucible, it is possible to convert 0.5 g of calcium carbonate to oxide by heating 1 hour over a Tirrill burner.

Calcium oxide is hygroscopic but when strongly ignited there is no difficulty in weighing it provided that the above directions are followed. It is never safe to assume that the first weight is correct, however. If the cold crucible and its contents apparently gain weight rapidly while on the balance pan, it is probable that a little calcium chloride is present, owing to incomplete washing of the precipitate. This can be removed by moistening several times with ammonium carbonate and heating after each addition of carbonate.

Sometimes a little calcium sulfate is formed by allowing the gas flame to enter the crucible. This is not a serious source of error with the illuminating gas of most American cities.

If both solutions are not boiling hot during the precipitation, the calcium oxalate forms very fine crystals; it then settles very slowly and passes readily through the filter.

Calcium oxalate is inappreciably soluble in water and dilute acetic acid containing dissolved ammonium oxalate, but readily soluble in mineral acids. One liter of pure water dissolves 10 mg of calcium oxalate.

The precipitate, when formed in a boiling solution, corresponds to the formula $CaC_2O_4 \cdot H_2O$. It can be weighed in this form after drying at $100-105°$ or after washing with alcohol and ether. Before washing with alcohol, the precipitate must be washed well with hot water. One of the best ways to handle the precipitate is to dissolve it in acid and titrate with permanganate (see Chapter XV).

2. Determination of Calcium as Sulfate, $CaSO_4$

This method is chiefly used in the analysis of calcium salts of organic acids or for the conversion of calcium oxalate to sulfate in a porcelain crucible. For this purpose heat the calcium salt in a weighed crucible until the organic matter is destroyed. Then cover the crucible with a watch glass, add some dilute sulfuric acid, and heat upon the water bath until there is no longer any evolution of carbon dioxide. Wash off the under side of the watch glass and evaporate the liquid as far as possible on the bath. Then carefully expel excess of sulfuric acid by inclining the crucible and heating over the free flame (or in an air bath). Ignite gently and weigh. By strong ignition calcium sulfate loses SO_3.[1]

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[1] After heating for 1 hour to dull redness, 0.2652 g $CaSO_4$ remained unchanged in weight, but on heating with the full flame of a Tecla burner it lost 0.0004 g in weight. On heating for 1 hour over the blast lamp it lost 0.0051 g. (J. Weber.)

Calcium may also be precipitated as calcium sulfate. Treat the neutral solution containing about **0.1** g of calcium in 25 ml with 2 ml of 6 N sulfuric acid, add 4 volumes of alcohol, and allow the mixture to stand 12 hours. Filter, wash with **70** per cent alcohol, gently ignite in a crucible, and weigh.

3. Determination of Calcium as Carbonate, $CaCO_3$

Only rarely is calcium precipitated as carbonate by ammonium carbonate in the presence of ammonia. Gently ignite the filtered and washed precipitate and weigh as carbonate. After weighing, moisten the residue with a little ammonium carbonate solution, evaporate to dryness on the water bath, and again ignite gently. This is done in order to change small amounts of calcium oxide, which may have been formed during the burning of the filter paper, back to carbonate.

In the presence of considerable ammonium chloride the precipitation of calcium by means of ammonium carbonate is never complete whereas the precipitation with ammonium oxalate always is.

If a calcium oxalate precipitate is ignited to constant weight in a porcelain crucible at a temperature ranging from 675° to 800°, while a current of dry carbon dioxide is constantly being led into the crucible, the precipitate is converted into calcium carbonate.[1] To obtain a suitable temperature range, heat the precipitate in a 30-ml Gooch crucible, covered with a Rose crucible cover and resting in a 15-ml porcelain crucible which is heated with the full heat of a Bunsen burner. Under these conditions potassium iodide (m.p. 685°) should melt in the Gooch crucible and potassium chloride (m.p. 790°) should not. Heat the crucible slowly at first to dry the precipitate and then with the full heat of the burner for 15 minutes, continuing the current of carbon dioxide until the crucible is nearly cold.

STRONTIUM, Sr.   At. Wt. 87.63

Forms: $SrSO_4$, $SrCO_3$, SrO

The determination as the sulfate is the most accurate.

Determination of Strontium as Sulfate, $SrSO_4$

Procedure. To 100 ml of the neutral solution containing not more than 0.5 g of strontium add **5 ml** of 6 N sulfuric acid and as much alcohol as there is volume of solution. Stir well, allow the mixture to

[1] H. W. Foote and W. M. Bradley, *J. Am. Chem. Soc.*, 48, 676 (1926).

stand 12 hours, filter and wash, at first with 50 per cent alcohol to which a little sulfuric acid has been added, and finally with pure alcohol until the wash water no longer gives the sulfuric acid reaction. Dry, ignite, cool, and weigh.

Remarks. Only about 0 014 g of SrSO₄ dissolves in 100 ml of pure water. The addition of a little sulfuric acid decreases the solubility, but if too much acid is added, the precipitate dissolves appreciably.

It is very soluble in concentrated sulfuric acid and appreciably soluble in dilute hydrochloric and nitric acids, acetic acid, and in concentrated solutions of magnesium or alkali chloride.

If considerable acid is present it should be removed by evaporation.

Determination of Strontium as Oxide, SrO, or as Carbonate, SrCO₃

Precipitate the strontium as carbonate, or as oxalate, and change by ignition to the oxide as described under "Calcium."

Strontium carbonate is decomposed by heat with more difficulty than calcium carbonate, and the determination as carbonate is very satisfactory. It is advisable to treat the precipitate as described under "Calcium," although it is usually unnecessary to heat with additional ammonium carbonate.

Solubility of Strontium Carbonate in Water according to Fresenius

At ordinary temperatures, 18,045 parts of water dissolve 1 part of SrCO₃. *In water containing ammonium carbonate the salt is much less soluble;* on the other hand, ammonium chloride and ammonium nitrate increase its solubility. If calcium, strontium, magnesium, and alkali salts are present together, as in minerals and in mineral waters, the calcium and strontium are both precipitated as oxalates and transformed by ignition into the oxides Cf. pp. 244, 246.

Solubility of Strontium Oxalate in Water

At ordinary temperatures, 12 l of water dissolves 1 g of SrC₂O₄ 2½H₂O. The solubility is very much less in water containing ammonium oxalate.

BARIUM, Ba. At. Wt. 137.36

Forms: BaSO₄, BaCrO₄

1. Determination as Barium Sulfate

Dilute the solution so that it contains not more than 0.15 g of barium per 100 ml. Make slightly acid with hydrochloric acid, heat to boiling, and add a slight excess of hot, normal sulfuric acid. Use about 3 ml of normal acid for each 100 ml of solution. After the precipitate has settled, add a little more sulfuric acid to make sure that the precipitation is complete. After allowing to stand for an hour or more in a

warm place, decant the solution through a filter and wash 4 times by decantation with 50-ml portions of hot water containing a few drops of sulfuric acid. Finally transfer the precipitate to the filter and wash with hot water till free from acid. Ignite the wet precipitate and filter in a platinum or porcelain crucible. Do not heat over the blast lamp or Méker burner, because barium sulfate is decomposed at about 900°. Cool in a desiccator and weigh as $BaSO_4$.

The precipitate usually contains a little chloride and the results are likely to be somewhat low. Sometimes a low result is caused by too rapid combustion of the filter which causes the formation of barium sulfide. To correct both of these errors, moisten the precipitate with a few drops of $18 N$ sulfuric acid, carefully evaporate off the acid, gently ignite, and weigh again. Repeat the treatment until two successive weighings agree within 0.3 mg.

Remark. It is difficult to get pure precipitates of barium sulfate.[1] One liter of pure water dissolves only about 3 mg of barium sulfate, and it is even less soluble in water containing a little sulfuric acid. It is appreciably soluble in solutions containing more than 1 ml of 6 N mineral acid per 100 ml and is very soluble in concentrated sulfuric acid. A full discussion of the problem of producing pure precipitates of barium sulfate is given under "Sulfuric Acid" in Chapter XI.

The formation of a little barium sulfide during the ignition of the precipitate does not usually cause error, for it is easily roasted back to sulfate by beating the inclined crucible with a small flame at the back so that there is ready access of air into the crucible.

2. Determination of Barium as Chromate

Dilute the neutral solution, containing not more than 0.4 g of barium, to 200 ml, add 10 drops of 6 N acetic acid, heat to boiling, and slowly add a slight excess of ammonium chromate solution. Prepare the reagent by dissolving 12.5 g of ammonium dichromate in 100 ml of water and adding ammonium hydroxide until the color is a clear yellow. Allow the precipitate of barium chromate to settle, and make sure that the precipitation is complete by adding a little more reagent. When cold, filter through a Gooch or Munroe crucible and wash with hot water until 20 drops of the filtrate give scarcely any reddish brown coloration with a neutral solution of silver nitrate. Dry the precipitate in the hot closet, and then heat within a larger porcelain crucible (cf. p. 31) until the precipitate becomes a bright yellow.[2] Cool and weigh as $BaCrO_4$.

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[1] Cf. M. J. van't Krys, Z. anal. Chem., 1910, 393.

[2] Often some of the precipitate is reduced to chromic oxide by traces of organic matter, whereby it appears slightly greenish. By long-continued ignition in an open crucible the chromic oxide is changed back to chromate, and the precipitate appears a homogeneous yellow throughout.

Solubility of Barium Chromate[1]

The solubility product of barium chromate at room temperature is 2.0×10^{-10}, which means that the saturated solution contains about 3.5 mg $BaCrO_4$ per liter. The salt is about four times as soluble in boiling water. This solubility is somewhat greater than that of barium sulfate, whose solubility product is 1.0×10^{-10}. Barium chromate is somewhat more soluble in solutions of ammonium acetate or ammonium nitrate but it is much less so in solutions containing ammonium chromate.

The second hydrogen of H_2CrO_4 has an ionization constant of 1.0×10^{-7}. For this reason, barium chromate unlike barium sulfate dissolves readily in dilute mineral acids and 1 l of 10 per cent acetic acid dissolves 0 055 g $BaCrO_4$.

SEPARATION OF THE ALKALINE EARTHS FROM MAGNESIUM AND FROM THE ALKALIES

I. Separation of Calcium from Magnesium (and Alkalies)

The separation of calcium from magnesium depends upon the different solubilities of the two oxalates. Less than 0.2 mg of $CaC_2O_4 \cdot H_2O$ is dissolved by 1 liter of hot, 0.25 per cent ammonium oxalate solution, but the same quantity of hot water will dissolve 1 g of $MgC_2O_4 \cdot 2H_2O$. Twenty grams of $(NH_4)_2C_2O_4 \cdot H_2O$ will not interfere with the complete precipitation of calcium but, even in the presence of calcium, will prevent precipitation of Mg^{++} when as much as 2.7 g of $MgCl_2 \cdot 6H_2O$ is present in 100 ml of solution.[2]

It has been known for a long time that, when calcium oxalate is precipitated in the presence of magnesium ions, particularly when the solution has remained for a long time in contact with the precipitate, some magnesium is likely to be found in the precipitate. This has been attributed to the formation of a solid solution of magnesium oxalate in calcium oxalate, to adsorption or occlusion of magnesium oxalate,[3] or to the gradual breaking down of a supersaturated solution of magnesium oxalate.[4] For this reason it is quite generally believed that a precipitate of calcium oxalate formed in the presence of magnesium ions is rarely, if ever, pure,[5] and therefore it is customary to filter off the precipitate, redissolve it in acid, and reprecipitate whenever the content of magnesium amounts to more than a few *milligrams*. Bach and W Fresenius,[6] however, have apparently proved that Richards[7] was right in asserting that the separation is accurate if the proper conditions are maintained.

For the precipitation of small quantities of calcium in the presence of much magnesium, three methods have been proposed. (1) The calcium oxalate is formed in the usual way; the precipitate is filtered off, dissolved, and reprecipitated a second and a third time. (2) The calcium oxalate is precipitated in the presence of ammonium salt using only a slight excess of ammonium oxalate over that required by the

[1] Cf P. Schweizer, *Z. anal. Chem.*, 1890, p. 414, and R. Fresenius, *ibid.*, 1890, p. 418.
[2] Bobtelsky and Malkowa-Janowski, *Z. angew Chem.*, 40, 1437 (1927).
[3] T. W. Richards, *Z anorg. Chem.*, 28, 701 (1901).
[4] W. M. Fischer, *Z. anal. Chem*, 163, 62 (1926).
[5] Cf. Lundell and Knowles, *J. Am. Ceramic Soc.*, 10, 834 (1927).
[6] *Chem. Ztg.*, 49, 514 (1926).
[7] *Loc. cit.*

calcium. (3) The calcium oxalate is precipitated in 100 ml of solution by the addition of 20 g of ammonium oxalate; the hot solution is filtered off after standing a short time, and no attention is paid to any precipitate of magnesium oxalate that forms in the cold filtrate after some time. When the last method is used, the excess ammonium salts must be removed before attempting to precipitate $MgNH_4PO_4\cdot6H_2O$.

Procedure. Dilute the slightly acid solution with hot water so that not more than 0.3 g of either calcium or magnesium is present in 300 ml. Add 10 g of ammonium chloride, if not already present, heat to 80–90°, and slowly add, while stirring, an aqueous solution of 2 g of $(NH_4)_2C_2O_4\cdot H_2O$. Add ammonium hydroxide until the solution is slightly ammoniacal and allow the solution to stand an hour, but not much longer, before filtering. Filter, wash with hot water, and continue as described under "Calcium."'

II. Separation of Strontium from Magnesium

This separation finds practical application in the analysis of almost all mineral waters and of minerals containing strontium. In all these cases, however, strontium occurs in relatively small amounts in the presence of large amounts of calcium and varying amounts of magnesium, so that it is a question, first, of separating calcium and strontium from magnesium. This separation is effected by the precipitation of the calcium and strontium as oxalates as described on p. 244.

The filtrate containing magnesium may also contain traces of strontium. Remove ammonium salts by evaporating to dryness and heating the residue, dissolve this in hydrochloric acid, add sulfuric acid and alcohol, and allow the solution to stand for 12 hours. Filter off any resulting precipitate, consisting of strontium or barium sulfate, and weigh. From this filtrate precipitate the magnesium as magnesium ammonium phosphate as described on pp. 256–259, and weigh as the pyrophosphate or as $MgNH_4PO_4\cdot6H_2O$.

III. Separation of Barium from Magnesium

If it is desired to separate only barium from magnesium, make the solution acid with hydrochloric acid, heat to boiling, and precipitate the barium by the addition of boiling, dilute sulfuric acid (cf. p. 247). A large excess of sulfuric acid must be avoided. Precipitate the magnesium in the filtrate as magnesium ammonium phosphate in the usual way.

In most cases, however, a separation of barium, strontium, and calcium from the magnesium is involved. Precipitate the three alkaline earths as oxalates as described for the separation of calcium from magnesium. A few milligrams of barium will escape precipitation. To recover this, add a little ammonium sulfate to the hot solution, filter, wash, and weigh as $BaSO_4$. In the filtrate, determine the magnesium as pyrophosphate or as $MgNH_4PO_4\cdot6H_2O$ (pp. 256–259).

IV. Separation of the Alkaline Earths from One Another

Principle. The mixture of the dry nitrates is treated with ether-alcohol, which dissolves calcium nitrate alone. The residue is taken up in water, the barium is precipitated as chromate, and the strontium is determined in the filtrate as sulfate.

(a) Separation of Calcium, Strontium, and Barium according to Rose-Stromeyer-Fresenius

Procedure. The three metals are assumed to be present together in solution in the form of their nitrates. Evaporate the solution in a small Erlenmeyer flask, as described under "Lithium," p. 284, while passing a stream of dry, warm air through the flask. When all the water is evaporated, raise the temperature of the oil bath to 140° and maintain this temperature for 1 to 2 hours, still passing the current of warm air through the flask. Cool, treat the dry residue with 10 times its weight of absolute alcohol, stopper the flask, and allow it to stand with frequent shaking for 1 to 2 hours. Add an equal volume of ether, close the flask, shake, and allow it to stand 12 hours. Filter through a filter moistened with ether-alcohol and wash with ether-alcohol until a few drops of the filtrate evaporated on platinum-foil leave no residue.

Evaporate the filtrate to dryness on a lukewarm water bath, dissolve the calcium nitrate in water, precipitate as the oxalate, and, after ignition, weigh as the oxide.

Remark. If only a small amount of calcium is present (not more than about 0 5 g) the above separation is complete. With large amounts of calcium, the residue of strontium and barium nitrates almost always contains some calcium In this case evaporate the aqueous solution again to dryness in the same way as before and repeat the treatment with alcohol and ether. Determine the calcium in the combined filtrates.

(b) Separation of Barium from Strontium according to Fresenius[1]

Requirements. 1. Ammonium chromate solution. Dissolve 100 g of ammonium dichromate (free from sulfate) in 500 ml of water, add 135 ml of 6 N ammonium hydroxide solution, filter if necessary, and dilute to 1 l.

2. Ammonium acetate solution. Dissolve 231 g in 1 l of water, or mix equal volumes of 6 N acetic acid and 6 N ammonia, leaving the solution slightly ammoniacal rather than acid.

3. Acetic acid, 6 N.

4 Nitric acid, 2 N.

Procedure. Dissolve the residue of strontium and barium nitrates obtained after the above treatment with ether-alcohol in a little water and dilute the solution until the concentration corresponds to about 1 g of mixed nitrates in 300 ml, heat to boiling, add 10 drops of acetic acid and about 10 ml of ammonium chromate solution (this should be an excess over the theoretical amount necessary), and allow to stand 1 hour. Wash the precipitate of barium chromate by decantation, with

[1] *Z. anal. Chem.*, 29, 427 (1890); 44, 742 (1906).

water containing 25 ml of ammonium chromate solution per liter, until the wash water no longer gives a precipitate with ammonia and ammonium carbonate; then wash with hot water containing 25 ml of ammonium acetate solution per liter until the last washing gives only a slight reddish brown coloration with neutral silver nitrate solution.

The precipitate on the filter still contains a little strontium. Carefully wash it back into the vessel in which the precipitation took place, and dissolve any precipitate remaining on the filter in a little hot 2 N nitric acid, allowing it to run through the filter vessel containing the precipitate. Wash the filter with hot water till free from acid. Heat the precipitate till it dissolves in the dilute nitric acid (about 6 ml is usually sufficient). Dilute the solution to 200 ml, heat to boiling, add 5 ml of ammonium acetate solution, little by little, and finally enough ammonium chromate solution to cause the disappearance of the odor of acetic acid from the solution (usually about 10 ml is necessary). After it has stood for 1 hour pour the liquid through a Gooch crucible, cover the residue in the dish with hot water, allow to cool, filter and wash with cold water until the filtrate gives only a slight opalescence with neutral silver nitrate. Dry the precipitate, ignite gently in an air bath (cf. p. 31), and weigh as $BaCrO_4$.

Add 1 ml of 6 N nitric acid to the filtrate, concentrate somewhat, and precipitate the strontium as carbonate by the addition of ammonia and ammonium carbonate. The precipitate always contains some strontium chromate. Wash it once with hot water, dissolve in hydrochloric acid, and determine the strontium as sulfate, according to p. 246.

The results obtained according to this method are very satisfactory.

(c) Separation of Calcium, Strontium, Barium, and Magnesium by the Method of E. H. Swift[1]

Instead of removing the calcium first by treatment with alcohol and ether, the barium is precipitated first as chromate from a dilute acetic acid solution which is buffered with ammonium acetate. Then, by making the solution ammoniacal, the strontium is precipitated as chromate and in this filtrate the calcium is precipitated as oxalate. If magnesium is present, it is found in the last filtrate and can be precipitated as magnesium ammonium arsenate. The procedure is easier to carry out than the separation by means of alcohol and ether, and the results are, on the whole, more satisfactory.

[1] The method is based on the work of W. C. Bray (*J. Am. Chem. Soc.*, 31, 611 [1909]). It is similar to the qualitative procedure which was described in the first volume of this book. The method has been modified by E. H. Swift in his *System of Chemical Analysis* as a result of experiments made at the California Institute of Technology.

Precipitation of Barium. To the dilute acid solution, such as is obtained by dissolving the carbonates of barium, strontium, calcium, and magnesium in nitric acid, add strong ammonia until the solution reacts basic and then add nitric acid dropwise until the solution is barely acid to litmus. Evaporate, without boiling, to about 35 ml, add exactly 1 ml of 6 N acetic acid from a 1-ml pipet and 10 ml of neutral 3 N ammonium acetate solution. Heat nearly to boiling and, while shaking, add dropwise sufficient K_2CrO_4 solution (292 g per liter) to impart a yellow color to the solution; 3 ml of the reagent is sufficient for 500 mg of Ba. Allow the precipitate of $BaCrO_4$ to settle completely and then filter. If there is much precipitate, keep as much of it as possible in the flask and wash with three 10-ml portions of hot water. Reserve the filtrate for the determination of strontium, calcium, and magnesium.

Dissolve the precipitate in 7–15 ml of cold 3 N HCl poured through the filter into the flask in which the precipitation took place. When all the precipitate in the flask has dissolved, wash the filter with several small portions of hot water, added at the top of the filter. Add 1 ml more of the K_2CrO_4 reagent; add ammonia dropwise until the color changes from orange to yellow and then 2 ml more. Add 6 N acetic acid until the original orange color returns, heat nearly to boiling, allow the precipitate to settle, and decant through a filter after 5 minutes. Wash the precipitate with four 5-ml portions of hot water.

Determination of Barium. Dissolve the precipitate in just 10 ml of cold 6 N HCl added dropwise to the top of the filter and running into the flask which contains the bulk of the $BaCrO_4$ precipitate. Wash the filter with four 10-ml portions of water. Break up the precipitate and swirl the solution until the precipitate dissolves, add 2–3 g of KI, allow to stand in the dark for 5 minutes, and then titrate the liberated iodine with 0.1 N $Na_2S_2O_3$ (see " Iodimetry " in Chapter XV).

Precipitation of Strontium. To the combined filtrates from the two $BaCrO_4$ precipitations, which should be reduced if necessary to a volume of 60 ml, add strong ammonia until the color changes from orange to yellow and 5 ml in excess. Add 3 ml more of the K_2CrO_4 reagent, cool, and to the cold solution add 30 ml of 95 per cent ethyl alcohol. If more than 100 mg of strontium is present add 3 ml more of the K_2CrO_4 reagent and 10 ml more of alcohol. Let the mixture stand 10 minutes and then decant the solution through a filter. Without washing the precipitate dissolve it in 5–10 ml of hot 6 N acetic acid and wash the filter with hot water. Neutralize the solution with ammonia and add 2 ml of concentrated ammonia in excess. Dilute to 30 ml; add 2 ml more of the K_2CrO_4 reagent and 20 ml of 95 per cent ethyl alcohol.

Filter after allowing to stand for 30–60 minutes. Wash the precipitate with a mixture of 1 ml concentrated ammonia and 10 ml of 50 per cent alcohol, added in small portions. Save the combined filtrates for the determination of calcium and magnesium.

Determination of Strontium. Dissolve the $SrCrO_4$ precipitate on the filter in 3–5 ml of 6 N acetic acid and catch the solution in the flask which contains the bulk of the light yellow precipitate. Wash the filter with 10–20 ml of hot water. Heat the acid in the flask until the $SrCrO_4$ precipitate dissolves, dilute to 50 ml, and heat to boiling.

To the boiling solution add 3–5 ml of 3 N $K_2C_2O_4$ solution, make slightly ammoniacal, and add 5 ml of ammonia in excess. Boil very gently for 5 minutes, cool, and allow the $SrC_2O_4 \cdot H_2O$ precipitate to settle. Decant the solution through a filter and wash the precipitate with 5-ml portions of hot 0.6 N NH_4OH solution. Dissolve the precipitate in 50 ml of hot 3 N HCl and wash the filter with 50–75 ml of hot water. Titrate the oxalic acid at 70–80° with 0.1 N $KMnO_4$ after adding 10 ml of the Zimmermann-Reinhardt "preventive solution." (See Chapter XV.)

Precipitation of Calcium. Precipitate the calcium in the filtrate from the $SrCrO_4$ precipitation as described on p. 244. The determination can be finished as described there or the oxalic acid can be titrated with $KMnO_4$ after dissolving the $CaC_2O_4 \cdot H_2O$ in dilute sulfuric acid as described under "Determination of Calcium" in Chapter XV.

Determination of Magnesium. Magnesium can be determined in the filtrate from the $CaC_2O_4 \cdot H_2O$ precipitate as described on p. 257 or 259, but if it is preferred to determine the magnesium by titration it can be precipitated as $MgNH_4AsO_4 \cdot 6H_2O$.

To the filtrate from the calcium oxalate precipitation, add 10 ml of concentrated ammonia and 10–25 ml of a solution containing 312 g of $Na_2HAsO_4 \cdot 7H_2O$ per liter. Allow the precipitate to settle over night. Filter and wash the $MgNH_4AsO_4 \cdot 6H_2O$ precipitate with 1.2 N NH_4OH until a 5-ml portion of the wash water gives no precipitation upon the addition of 1 drop of N $Ca(NO_3)_2$ reagent.

Dissolve the precipitate in 20–50 ml of 6 N HCl. If more than 50 mg of Mg is present, dilute the solution with 6 N HCl to exactly 100 ml in a volumetric flask. Mix and take a portion of the solution containing 30–40 mg of Mg for further analysis by means of a pipet or buret. To the solution in a glass-stoppered bottle add not more than 1 g of solid $NaHCO_3$ in small portions and 1 g of KI. Allow the contents of the stoppered flask to stand 5 minutes, add 3–5 ml of CCl_4, and titrate very slowly with 0.1 N $Na_2S_2O_3$ until, after shaking, no iodine is present in the CCl_4, as shown by the absence of color.

This titrimetric determination of magnesium is based on the reduction of arsenate to arsenite. The reduction by means of potassium iodide takes place completely only when the solution is about 6 N in HCl. The solution must be titrated slowly as there is some danger of the strong acid reacting with sodium thiosulfate to form sulfurous acid and sulfur; the sulfurous acid then reacts with twice as much iodine as the original thiosulfate does. The addition of the sodium bicarbonate is to provide an atmosphere of CO_2 and prevent oxidation of the iodide by atmospheric oxygen. There is some danger that a precipitate of red AsI_3 may form if much KI is added.

In the final titration, 1 ml of 0.1 N $Na_2S_2O_3$ reacts with arsenic acid equivalent to 0.001216 g Mg or 0.002016 g MgO.

GROUP V OF CATIONS

MAGNESIUM, POTASSIUM, SODIUM, LITHIUM, AND AMMONIUM

MAGNESIUM, Mg.   At. Wt. 24.32

Forms: $MgSO_4$, $Mg_2P_2O_7$, $MgNH_4PO_4 \cdot 6H_2O$, $Mg(C_9H_6NO)_2$

(a) Determination as $MgSO_4$

This method for the determination of magnesium can always be employed when the magnesium is combined with an acid which can be volatilized by heating with sulfuric acid, and when no basic constituent other than ammonium and magnesium is present.

Place 0.5 g of the substance in a crucible and add about 2 ml of concentrated sulfuric acid. Substances which react violently with concentrated H_2SO_4 should be first treated with water, and dilute sulfuric acid added little by little. Evaporate on the water bath as far as possible; dry at 110-120°; and remove the excess of sulfuric acid by cautiously heating the crucible, held in an inclined position, over a free flame. Finally, heat the dry mass just to redness in a covered crucible, cool in a desiccator, and weigh as quickly as possible, as the anhydrous magnesium sulfate is hygroscopic.

(b) Determination as Magnesium Pyrophosphate

This, the most important of all the methods for the determination of magnesium, is always applicable and depends upon the following principles: If the solution of a magnesium salt is treated with an alkali orthophosphate solution in the presence of ammonium chloride and ammonia, the magnesium is completely precipitated as magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$, which by ignition is changed to magnesium pyrophosphate:

$$2MgNH_4PO_4 \cdot 6H_2O = 2NH_3 + 13H_2O + Mg_2P_2O_7$$

Formerly it was common practice to precipitate magnesium ammonium phosphate in the cold. Neubauer[1] showed, however, that this sometimes leads to high

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[1] Z. angew. Chem., 1896, 439. See also Gooch and Austin, Z. anorg. Chem., 20, 121.

results and at other times the results are low. They are low when the precipitation takes place in strongly ammoniacal solutions containing but little ammonium salts, particularly when the phosphate solution is added slowly. Tribasic magnesium phosphate, $Mg_3(PO_4)_2$, contaminates the precipitate. On the other hand, the results are too high if the precipitation takes place in neutral or slightly ammoniacal solution in the presence of considerable ammonium salts. In this case more or less monomagnesium ammonium phosphate, $Mg(NH_4)_4(PO_4)_2$, is formed. This compound is changed to magnesium metaphosphate by gentle ignition

$$2Mg(NH_4)_4(PO_4)_3 = 2Mg(PO_3)_2 + 8NH_3 + 4H_2O$$

Sometimes, when considerable ammonium salt is present, no precipitation takes place on the addition of the ammonia, but usually the precipitate will appear after standing over night in the presence of 2.5 N NH_4OH, which is the approximate concentration obtained by following the above directions. Besides the treatment described on p. 266, three other methods can be recommended for removing ammonium salts. (1) Evaporate the solution to dryness in a porcelain casserole, and heat the dry residue until no more vapors of ammonium salt are evolved. Cool, moisten the residue with 5 ml of 6 N hydrochloric acid, heat till basic salts are dissolved, dilute to about 25 ml, filter and wash the filter with hot water until free from chloride. Add 5 ml of concentrated hydrochloric acid and some alkali phosphate. Dilute the solution to about 125 ml, heat nearly to boiling, and neutralize with ammonia as directed on p. 258. (2) Evaporate the solution to dryness after adding some nitric acid. To the residue add 25 ml of water, 50 ml of concentrated nitric acid, and 15 ml of concentrated hydrochloric acid, and again evaporate to dryness.[1] By this treatment with aqua regia, ammonium salts are oxidized to nitrogen. Finally treat this residue with 5 ml of 6 N HCl and 20 ml of water. Heat for a few minutes to dissolve basic salts and filter into a 250-ml beaker. Wash the filter with hot water till free from chloride, add 5 ml of concentrated hydrochloric acid, dilute to 125 ml, add 1 2 g of diammonium phosphate, and precipitate with ammonia as described on p. 258. (3) To the neutral solution add 5 g of sodium acetate and an excess of bromine water Heat carefully, and add more bromine until finally all the ammonium salt is oxidized. The reaction

$$2NH_4^+ + 3Br_2 + 6C_2H_3O_2^- \rightarrow N_2 + 6Br^- + 8HC_2H_3O_2$$
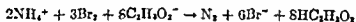
will take place provided that sufficient sodium acetate anion is present to keep the solution buffered.

Method of B. Schmitz[2]

If the original volume is over 300 ml it is well to concentrate the *acid* solution by evaporation on the hot plate. If the solution is accidentally evaporated to dryness, moisten the residue with 5 ml of 6 N hydrochloric acid and enough water to dissolve ammonium salts, which are always present when the magnesium is determined in the filtrate from the precipitation of calcium oxalate. If a clear solution is not obtained, heat to boiling and filter if necessary. Wash the pre-

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[1] J. Lawrence Smith, *Am. J. Sci.*, **15**, 94 (1853).

[2] *Z. anal. Chem.*, **65**, 46 (1924)

cipitate (usually a little silica from the glass) once with 2 N hydrochloric acid and then with hot water till free from chloride.

To the acid solution add 5 g of ammonium acetate, an excess of ammonium phosphate, and a few drops of phenolphthalein solution. Heat the solution to near the boiling point and then slowly add 1.5 N ammonia water until a faint pink color is obtained and a slight precipitation takes place. Stir well for about a minute, touching the sides of the beaker as little as possible. When the precipitate has become distinctly crystalline, add more ammonia until a deep color is obtained with the phenolphthalein. Allow the solution to cool, then add one-fifth the solution's volume of concentrated ammonium hydroxide and allow to stand at least 4 hours, preferably over night.

Filter into a weighed Gooch crucible. Wash the precipitate with 1.5 N ammonia until free from chloride, and finally moisten it with 4-5 drops of a saturated solution of ammonium nitrate in 1.5 N ammonia. Ignite very slowly, gradually increasing the heat until the precipitate is white. After cooling, weigh the $Mg_2P_2O_7$:

$$2MgNH_4PO_4 = 2NH_3 + H_2O + Mg_2P_2O_7$$

From the weight of the latter, the content of magnesium or of magnesium oxide can be calculated.

The precipitate can be filtered upon an ashless filter paper, but the ignition must always be gradual, in order to obtain perfectly white pyrophosphate. By rapid ignition, some of the phosphorus is reduced by the ammonia. This reduction is likely to injure a platinum crucible. Often a black precipitate can be whitened by moistening with strong nitric acid and carefully heating. This treatment, however, should be avoided by carefully igniting the precipitate.

The precipitate has the formula $MgNH_4PO_4 \cdot 6H_2O$ when formed in cold aqueous solutions It can be weighed in this form, and since it will then weigh about 2.2 times as much as the corresponding weight of $Mg_2P_2O_7$, a slight error in the final weight, such as is likely to occur in igniting the precipitate, has less effect upon the final result. Above 60°, the stable form is $MgNH_4PO_4 \cdot H_2O$, and it can be weighed as such after drying for an hour at 100° with fairly satisfactory results.

To weigh the precipitate with its six molecules of water, proceed as above but omit the treatment with ammonium nitrate solution. For filtering use a Gooch crucible which has been washed with alcohol and ether, as described below, and weighed.

After removing all soluble salts by washing with 1.5 N ammonia, wash the precipitate with four 5-ml portions of ethyl alcohol, draining well after each washing. This serves to remove nearly all the adhering water. Then wash the precipitate with four 5-ml portions of ether, draining after each washing and drawing air through the crucible for 5 minutes after the last washing. Then wipe off the outside of the cold crucible, allow it to stand in a desiccator for 20 minutes, and weigh. Students

find this method of handling the precipitate the easiest and quickest. The results are good. To make sure that all soluble salts have been removed, wash the weighed precipitate with some 1.5 N ammonia, and then with alcohol and ether as before. The new weight should agree with that first obtained.

Method of Epperson[1]

To the neutral or slightly acid solution of magnesium chloride, containing not more than 0.1 g of MgO and having a volume of about 150 ml, add 5 ml of concentrated hydrochloric acid and some methyl red indicator solution. Add 10 ml of 20 per cent $(NH_4)_2HPO_4$ solution and, while constantly stirring, concentrated ammonium hydroxide until the solution contains 5 ml more of this reagent than enough to make the solution neutral. Allow the solution to stand at least 4 hours or preferably over night. Filter and wash with 1.5 N ammonium hydroxide. Dissolve the precipitate on the filter by washing it alternately with small portions of hot 1.5 N hydrochloric acid and hot water. Add 1 ml of the ammonium phosphate solution and repeat the precipitation of magnesium ammonium phosphate as before in a volume of 100–150 ml. Allow the precipitate to stand at least 4 hours, filter, and wash with 1.5 N ammonium hydroxide until free from chloride, and then moisten with 4–5 drops of a saturated solution of ammonium nitrate in 1.5 N ammonium hydroxide. Ignite carefully at approximately 500°, taking care not to let the filter paper take fire, until the precipitate of $Mg_2P_2O_7$ is white, and finally at 1000° to constant weight.

By this double precipitation a normal precipitate is obtained. The precipitate can be weighed as $MgNH_4PO_4 \cdot H_2O$ or as $MgNH_4PO_4 \cdot 6H_2O$ (cf. p. 258).

(e) Determination of Magnesium with 8-Hydroxyquinoline

8-Hydroxyquinoline, for which the trivial name oxine has been proposed, has the empirical formula HO C_9H_4N and the structural formula. The hydrogen of the OH group is replaceable by metal, and precipitates are produced under suitable conditions when the reagent is added to solutions containing ions of magnesium, aluminum, copper, bismuth, cadmium, zinc, mercuric mercury, lead, antimony, tin, vanadium, uranium, iron, titanium, zirconium, tantalum, columbium, manganese, nickel, or cobalt. The reagent, therefore, is not specific for any particular ion, but the solubility of the various precipitates varies enough so that it can be used for numerous separations. None of the precipitates are formed from strongly acid solutions. Some of them are formed from solutions containing acetic acid and alkali

[1] Alice Whitson Epperson, *J. Am. Chem. Soc.*, 50, 324 (1928).

acetate, some from solutions which are ammoniacal, and still others from solutions which are made alkaline with sodium hydroxide. Magnesium hydroxyquinolinate is much less soluble than the corresponding calcium compound, and pure precipitates of the magnesium compound can be obtained in the presence of small quantities of calcium. The greenish yellow precipitate is crystalline, easy to handle, and forms somewhat more readily than does magnesium ammonium phosphate, but, as with that compound, large quantities of ammonium salt, especially ammonium oxalate, prevent its formation. The precipitate can be weighed as $Mg(C_9H_6ON)_2 \cdot 2H_2O$ after drying at 105° or without the water of crystallization after drying at 140°. Instead of weighing the precipitate, it can be dissolved in dilute hydrochloric acid and titrated with $KBrO_3$-KBr solution, in which case each atom of magnesium is equivalent to 8 atoms of bromine, as the following equations show:

$$Mg(C_9H_6ON)_2 \cdot 2H_2O + 2HCl = MgCl_2 + 2C_9H_7ON + 2H_2O$$
$$C_9H_7ON + 2Br_2 = C_9H_5ONBr_2 + 2HBr$$
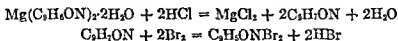
The Br is formed when the mixture of $KBrO_3$ and KBr comes in contact with acid:

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O$$

The end point of the titration can be determined with indigo carmine as indicator, or, as is better, an excess of the $KBrO_3$-KBr solution can be added, whereby an excess of Br_2 is provided which will react with KI and liberate iodine which can be titrated with

$Na_2S_2O_3$ (see "Iodimetry"). The formula of the bromine compound is

The following directions for determining magnesium as the hydroxyquinolinate will apply to a solution from which calcium has been removed as oxalate, as in the analysis of minerals [1]

Oxine Reagent. Dissolve 25 g of 8-hydroxyquinoline in 60 ml of glacial acetic acid. Dilute the solution with cold water to 2 l. One milliliter of this solution is equivalent to 0.0017 g of MgO.

Procedure. To 100 ml of solution containing 10–50 mg of magnesium add 2 g of NH_4Cl and 0.5 ml of 0.02 per cent solution of o-cresolphthalein. Neutralize with ammonia and add at least 2 ml of 6 N NH_4OH in excess. Heat to 70–80° and add the oxine solution until an excess is present as shown by the solution becoming deep yellow in color. Digest 10 minutes on the steam bath with frequent stirring. Filter through a weighed filtering crucible and wash with 50 ml of hot water. Dry at 105° for an hour, cool in a desiccator, and weigh. Repeat the heating for 0.5-hour periods until a constant weight is obtained. The precipitate is $Mg(C_9H_6NO)_2 \cdot 2H_2O$ and contains 6.988 per cent Mg or 11.56 per cent MgO. The use of a mechanical stirrer while the precipitate is forming is helpful but not absolutely necessary.

[1] Redmond and Bright, *Bur. Standards J. Research*, **6**, 113 (1931).

Titrimetric Determination. Dissolve the washed precipitate in 25 ml or more of 2 N HCl in a glass-stoppered bottle. Add 1 g of KBr and 1 ml of 0.01 per cent methyl red solution. Titrate slowly with 0.1 N KBrO$_3$ solution until an excess is present as shown by loss of color by the indicator. Add a little CCl$_4$, CHCl$_3$, or CS$_2$ and 2 g of KI. Titrate with 0.025 N Na$_2$S$_2$O$_3$ solution until, after shaking, no free iodine is shown to be present.

Analysis of Limestone, Dolomite, or Portland Cement

Portland cement is made by heating limestone with a clay rich in silica. The cement, therefore, contains the non-volatile constituents of both materials. It represents a silicate completely decomposable by dilute mineral acid. In the analysis of limestone, not much undecomposable silicate is likely to be present, and the three important determinations are: lime, CaO; magnesia, MgO; and carbon dioxide, CO$_2$. In a commercial analysis, the residue insoluble in dilute acid is often weighed and called "insoluble material"; the precipitate obtained with ammonium hydroxide is ignited and weighed as "combined oxides" consisting chiefly of Fe$_2$O$_3$ and Al$_2$O$_3$. In the analysis of portland cement the procedure is usually except that special care is necessary for the determination of the silica, the iron is usually determined, the corresponding weight of Fe$_2$O$_3$ is deducted from the ignited ammonium hydroxide precipitate, and the difference is called alumina. This precipitate may also contain a little manganese, titanium, and traces of silica and phosphoric anhydride. With portland cement, the determination of carbon dioxide is unimportant but sulfate is usually determined because a little gypsum is commonly used in the preparation of the cement, but the calcium sulfate content should be kept low and specifications are rigid with respect to this point. The testing of portland cement also includes certain physical tests in addition to the chemical analysis which alone concerns us here.

The American Society for Testing Materials has adopted a standard set of specifications[1] for portland cement, including its physical and chemical testing. The chemical methods recommended were those formulated by a committee who made a special study of this analysis. The following directions are based upon the report of the committee, but the procedure has been modified slightly in minor details and no attempt is made to reproduce the same wording. This scheme of analysis is given partly because of the technical importance of portland cement and partly because it has proved a satisfactory procedure to place in the hands of students as representative of a complete analysis.

The mode of procedure adopted by the above-mentioned committee called for two evaporations for the removal of the silica. In the discussion of the method, however, it was pointed out that, by heating the residue at 120°, not correcting for impurities by the hydrofluoric acid treatment and not correcting the subsequent precipitate formed by ammonia for small traces of silica, results are obtained which are within the permissible analytical error of the correct values. In fact, by this more rapid method, a compensation of errors takes place and the results are often better than if the same operator attempted to carry out the analysis with the utmost precision possible.

The committee also recommended the use of platinum dishes and platinum crucibles as far as possible. The advantages gained are obvious, but the price of platinum has become so high that it is the duty of every practical chemist to avoid the use of platinum utensils wherever possible. The errors introduced by using por-

celain instead of platinum are insignificant in most cases, although greater care must he taken to allow crucibles to cool before placing them in desiccators, and a longer time should elapse before weighing.

The original directions call for two precipitations of the calcium and for two precipitations of magnesium. This is unessential in the commercial testing of portland cement provided that the conditions recommended are carefully fulfilled. The directions apply equally well to the analysis of limestone.

Procedure. Weigh accurately to the nearest 0.1 mg about 0.5 g of limestone or cement into a 250-ml porcelain casserole, cover with 40 ml of water, and add 20 ml of 6 N hydrochloric acid, breaking up with a stirring rod any lumps that may form. Cover the casserole with a watch glass and digest about 15 minutes on a hot plate until the cement is decomposed completely. Rinse off the bottom of the cover glass with a little water and evaporate to dryness on the water hath. During the evaporation have the cover glass raised above the top of the casserole hy means of a glass support. Heat the casserole and dry the residue in a hot closet at 120°.[1]

Silica. Moisten the residue with 10 ml of 6 N hydrochloric acid, warm slightly, and add 150 ml of water. Cover the casserole with a watch glass and digest 10 minutes at a temperature near the boiling point. Filter into a 300-ml beaker; wash twice with 2 N hydrochloric acid and then with hot water till free from chloride. Transfer the moist precipitate, and filter to a weighed porcelain crucible with the paper folded so that the precipitate is entirely covered.[2] Smoke off the filter paper at a low heat without letting the paper take fire (cf. p. 40). Finally ignite at the full heat of the Méker burner until a constant weight is obtained of a perfectly white precipitate. Report as "insoluble residue" in the analysis of limestone or as "silica" in the analysis of portland cement.

Precipitation of Iron and Aluminum. To the filtrate and washings add ammonia solution until a slight ammoniacal odor persists after blowing away the vapors. Heat again just to boiling, and promptly filter off the precipitate of Fe(OH)₃ and Al(OH)₃. Wash the precipitate 6 times with small portions of hot water. Reserve the filtrate for the calcium and magnesium determinations.

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[1] At this temperature, the silica acid becomes dehydrated so that it is practically insoluble in dilute acids. The presence of the calcium chloride from the cement helps the dehydration. The quantity of silica that passes into the filtrate is negligible and more than balanced by that obtained from the reagents and dishes. The residue should not be baked too hard   At higher temperatures, combination of basic magnesium salt and silicic acid takes place and alumina is made very insoluble.

[2] Dry silica is very pulverulent and easily lost if the gases from the paper escape too violently, as when it takes fire.

Sometimes the precipitate contains a little calcium carbonate from the carbon dioxide in the air and often a little magnesium hydroxide. Wash the precipitate back into the casserole, place the casserole under the funnel, pour 5 ml of hot **3** N hydrochloric acid on the upper edge of the filter, and wash the filter with a little hot water. Continue the treatment with acid and water until all the precipitate left on the filter is dissolved. Finally wash the filter with a little dilute ammonia. Precipitate with ammonia just as before, filter through the original filter, and wash this second precipitate till free from chloride. Ignite ' the second precipitate wet in a porcelain crucible and weigh as $Fe_2O_3 + Al_2O_3$, neglecting the small quantities of TiO_2, P_2O_5, and Mn_3O_4 which it may possibly contain. Unite the filtrate with that obtained from the first precipitate.

In the analysis of limestone, the weight of this precipitate will usually be small. The iron content will often arise from a little ferrous carbonate present in the sample. Disregard this fact and simply report the percentage of " combined oxides " present.

In the analysis of portland cement, the precipitate after ignition should be largely Al_2O_3, and it is customary to regard it as $Al_2O_3 +$ a little Fe_2O_3. The quantity of the ferric oxide should be determined by titration, as follows:

Ferric Oxide. Transfer the ignited precipitate to a small beaker. Dissolve the traces that remain adhering to the crucible by heating small portions of 6 N hydrochloric acid in it, finally pouring each portion into the beaker. Use 20 ml of acid in all. Do not at any time dilute the hydrochloric acid until all the iron in the beaker is dissolved. Heat the acid with the iron and aluminum oxides at about 90° until all the iron has dissolved (cf. p. 170). When a clear solution is obtained, place the beaker on a filter, reduce carefully with stannous chloride, and determine the iron content by the Zimmermann–Reinhardt process (Chapter XV). Compute the percentage of Fe_2O_3 present, and subtract this from the above weight of the oxides to get the percentage of Al_2O_3.

Calcium Oxide. Make the combined filtrates acid with acetic acid, bring to a volume of about 400 ml, heat to 80–90°, and slowly add, while stirring, 30 ml of hot 0.5 N ammonium oxalate solution. Slowly add ammonium hydroxide until the solution is slightly ammoniacal, and allow the precipitate to stand an hour, but not much longer, before filtering.

If considerable magnesium is present in the solution, some magnesium oxalate will come down with the calcium oxalate. If, therefore, more than 10 per cent of MgO is present in the substance analyzed, it is best to redissolve the calcium oxalate precipitate and repeat the precipitation, using a paper filter for filtering off the precipitate. When all ,

the solution has passed through the filter, wash the precipitate with about 15 ml of hot water. Then rinse the precipitate back into the original beaker by holding the funnel in an inverted position and directing a stream of hot water against it. Replace the funnel in the support and wash the filter with about 25 ml of hot 3 N hydrochloric acid. Heat the acid in a test tube, pour it upon the upper edge of the paper, and catch the liquid as it runs through the filter in the beaker containing the precipitate. Finally wash the filter with a little hot water (and with dilute ammonia if it is to be used again for filtering the next precipitate). Heat the dilute acid in the beaker and add a little more acid if necessary to dissolve the precipitate completely. Dilute the solution to about 250 ml and repeat the precipitation of the oxalate at the boiling temperature, adding ammonia and 5 ml more of the ammonium oxalate reagent. Since the solution already contains oxalic acid equivalent to the calcium, only a little more reagent is necessary.

The calcium content of the precipitated calcium oxalate can be determined in various ways, all of which give good results.

1. The filtered precipitate corresponds to the formula $CaC_2O_4 \cdot H_2O$. It can be weighed in this form without difficulty because the water of crystallization is retained even after long heating at temperatures slightly above the boiling point of water.

2. It can be weighed as anhydrous calcium oxalate. To accomplish this it has been recommended that the precipitate be heated at 200-300° for some time.

3. It can be converted to calcium carbonate by heating to dull redness. The reaction

$$CaC_2O_4 \rightarrow CaCO_3 + CO$$

takes place at about 400°, but Foote and Bradley[1] have shown that it is safe to heat at 675-800° if the precipitate is in a tubulated crucible and a current of CO_2 is constantly led through the crucible while it is being heated. The common way of accomplishing the decomposition is to heat for some time to dull redness, cool, moisten with a little ammonium carbonate reagent, and again heat carefully until no more odor of ammonia is perceptible. For the first heating, 2 hours in a muffle at 500° has been recommended, and, after the treatment with ammonium carbonate solution, drying at 110° is sufficient.

4. After the ignition to calcium carbonate (and it does no harm if some calcium oxide is formed), the precipitate can be dissolved in a measured volume of 0.5 N hydrochloric acid and the excess acid titrated with 0.5 N sodium hydroxide to a methyl orange end point.

5. By strong ignition, calcium carbonate is changed to calcium oxide, which can be weighed. This method of handling the calcium oxalate precipitate is generally regarded as the best. Quantitative conversion can be accomplished in a covered platinum crucible by heating 1 hour with the full heat of a good Tirrill burner. The crucible should be covered loosely to prevent unnecessary loss of heat. A much shorter period of heating is necessary over a Méker burner or the blast lamp. A muffle heated to about 1000° can be used to advantage. The conversion of cal-

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[1] *J. Am. Chem. Soc.*, 48, 676 (1926).

cium oxalate to calcium oxide cannot be accomplished by heating in an open *porcelain* crucible over a Bunsen burner, and it requires a very long time to accomplish the conversion by heating in a covered porcelain crucible over a large Méker burner. The determination as oxide, therefore, is not to be recommended unless a muffle furnace or a platinum crucible is available.

6. The original calcium oxalate precipitate can be dissolved in dilute acid and the liberated oxalic acid titrated with potassium permanganate solution. This is one of the most popular methods and gives good results. For this method of analysis, the precipitate should not contain over 0 1 g of calcium. In portland cement analysis, therefore, an aliquot of the filtrate from the iron and alumina precipitation should be taken or an aliquot of the solution of the calcium oxalate precipitate in acid. To take an aliquot of any solution, dilute it to a definite volume in a volumetric measuring-flask. After diluting to the mark, mix the solution by pouring it back and forth at least four times, using a beaker which is clean and dry at the start. Then, by means of a pipet or a smaller measuring-flask take out at once one or more fractional parts of the entire solution for further analysis. Thus the filtrate from the ammonia precipitation can be diluted to exactly 500 ml, the solution mixed and 50 ml (= one-tenth) taken for the calcium determination. The word *aliquot* in mathematics designates a number that will divide a larger number without leaving a remainder In analytical chemistry it is used to represent an exact simple fraction of the whole sample taken for analysis.

Weighing as $CaC_2O_4 \cdot H_2O$. Use a weighed Gooch crucible for collecting the calcium oxalate precipitate. Wash the precipitate with hot 0.25 per cent ammonium oxalate solution until 3 ml of the washings gives no test for chloride on adding HNO_3 to an acid reaction and a few drops of $AgNO_3$ reagent. Then, with gentle suction, wash with six 5-ml portions of hot water, four 5-ml portions of ethyl alcohol, and four 5-ml portions of ether. Drain off each portion of wash liquid before adding more. Finally draw air through the washed precipitate for 5 minutes; wipe off the outside of the crucible and allow it to remain in a desiccator 15 minutes before weighing. The originally empty crucible should be washed, dried, and weighed in exactly the same way. The precipitate contains 38.39 per cent CaO. Save the filtrate for the determination of magnesium, preferably *without* the alcohol and ether washings.

Weighing as CaO. Use an ashless paper for collecting the precipitate. Wash the precipitate with hot water until free from chloride, and save the filtrate for the magnesium determination. Transfer the precipitate to a weighed *platinum* crucible. Ignite carefully with the flame at the mouth of the crucible until the precipitate is dry, and then heat with a small flame at the base of the crucible until all the paper is decomposed without letting it take fire. Then gradually raise the temperature and heat over a Tirrill burner for an hour with the crucible in an upright position and covered. Cool to about 100°, place in a desiccator, and weigh after 15 minutes. Repeat the heating until after cooling a constant weight is obtained. The calcium oxide is somewhat

hygroscopic but is not difficult to weigh if it has been washed free from chloride. Call the weight constant if it agrees within 0.2 mg with the previous weight.

Titration with Permanganate. Either a paper filter or a Gooch crucible can be used. After the precipitate has been washed free from chloride, transfer the precipitate together with the filter to a 400-ml beaker and dissolve the precipitate in 100-ml of warm 3 N sulfuric acid. Titrate at 70° with potassium permanganate as described in Chapter XV for the standardization of permanganate against sodium oxalate.

Magnesium Oxide. Make sure that the precipitation of $CaC_2O_4 \cdot H_2O$ was complete by adding 5 ml more of ammonium oxalate reagent.

At this stage, the solution will contain considerable ammonium salt. Ammonium salt is necessary to prevent the precipitation of $Mg(OH)_2$ with the hydroxides of iron and aluminum, and it also helps to prevent precipitation of MgC_2O_4. If the above procedure has been followed closely and only one precipitation of calcium oxalate made, which is permissible when the magnesium content is low, the magnesium can be precipitated as $MgNH_4PO_4 \cdot 6H_2O$ without removal of ammonium salts. It then is merely necessary to make the filtrate from the calcium oxalate precipitation acid with HCl, concentrate to about 300 ml by heating on the hot plate at a temperature somewhat below the boiling point, and precipitate with $(NH_4)_2HPO_4$ as will be described. If the solution should accidentally be evaporated to dryness, moisten the residue with strong HCl (to dissolve MgC_2O_4 or a basic salt), dilute to dissolve the ammonium salts, heat to boiling, and filter. Filtration is necessary because some silica is always present either from the reagents or from the action of the reagents on the beakers used.

Ammonium salts in small quantities are desirable in precipitating magnesium, but when considerable oxalate or ammonium chloride is present it will prevent precipitation of quite appreciable quantities of $MgNH_4PO_4 \cdot 6H_2O$. For that reason, magnesium is often missed in qualitative analysis, and it is quite common for chemists to report too low values for magnesium. It is safest always to remove excess ammonium salts by evaporating with nitric acid; the ammonium ion is oxidized to nitrogen gas. It is well to remember that approximately 6 N HCl and 15 N HNO₃ are constant-boiling acids, and approximately these concentrations are obtained when dilute solutions of these acids are evaporated.

Procedure. Add 75 ml of concentrated HNO_3 to the combined filtrates and washings from the $CaC_2O_4 \cdot H_2O$ precipitation, and evaporate to dryness on the steam bath or hot plate. Do not boil the solution or there will be loss by spattering. Keep the beaker covered with a watch glass supported above the upper rim of the beaker. A glass triangle, or glass supports which are made for this purpose, should be used to support the watch glass. To the small residue obtained, add 2 ml of concentrated HCl and 25 ml of water. Heat nearly to boiling, and, after a few minutes, filter off the silica residue through a small filter. Wash the beaker, and filter thoroughly with hot water. The silica comes from

the action of reagents on reagent bottles or on the beakers used in the analysis.

Dilute the solution to about 150 ml; add about 1.2 g of $(NH_4)_2HPO_4$ dissolved in a little water and a few drops of phenolphthalein indicator solution. Heat nearly to the boiling point, and then slowly add 1.5 N ammonia water until a faint pink color is obtained and a slight precipitation takes place. Stir well for about a minute, touching the sides of the beaker as little as possible. When the precipitate has become distinctly crystalline, add more ammonia until a deep color is obtained with the phenolphthalein. Allow the solution to cool, then add one-fifth the solution's volume of concentrated ammonium hydroxide and allow to stand over night. Continue the analysis by one of the following three procedures.

(a) **Weighing as $MgNH_4PO_4 \cdot 6H_2O$.** Prepare a Gooch crucible with a suitable asbestos mat for filtering. Rinse out the crucible under gentle suction, with four 5-ml portions of alcohol followed by four 5-ml portions of ether. Draw air through the crucible for 5 minutes to evaporate the ether, wipe off the outside with a clean cloth, allow to stand in a desiccator over calcium chloride for 15 minutes, and then weigh carefully. Decant off the mother liquor from the magnesium ammonium phosphate precipitate through this weighed crucible, wash the precipitate three times by decantation with 1.5 N NH_4OH (concentrated NH_4OH, d 0.90, diluted with nine times as much water), and transfer the precipitate to the crucible. Use a rubber policeman to remove the precipitate from the sides of the glass beaker. Wash the precipitate with the 1.5 N NH_4OH until the filtrate gives no test for chloride when made acid with nitric acid and treated with a few drops of silver nitrate solution. To collect filtrate for this test, place a test tube in the suction flask underneath the filter funnel. It is important that all the ammonium chloride should be washed out of the crucible before washing with alcohol and ether. Finally wash four times with 5-ml portions of alcohol, followed by four 5-ml portions of ether. Draw air through the crucible for 5 minutes, wipe off the outside of the crucible with a clean cloth, and weigh after it has remained in a desiccator 15 minutes. The precipitate contains 16.43 per cent of MgO.

(b) **Weighing as $MgNH_4PO_4 \cdot H_2O$.** Proceed exactly as in (a) but omit the treatment with alcohol and ether. After preparing the Gooch crucible with a suitable asbestos mat, place it in a small covered beaker and allow it to remain in the drying oven at 100° for at least an hour. Cool 15 minutes in a desiccator, and weigh carefully. After filtering off and washing the magnesium ammonium phosphate precipitate with 1.5 N NH_4OH till free from chloride, place the crucible in a small

covered beaker and allow it to remain an hour in the drying oven at 100°, but make sure that the oven does not exceed this temperature by more than one degree. The precipitate contains 15.65 per cent MgO.

The hexahydrate changes to the monohydrate at about 50°. While drying 1 hour at 100°, there is no appreciable decomposition of the monohydrate. If, however, the temperature is raised, or the precipitate is kept at this temperature for a long time, an appreciable decomposition takes place and there is a loss of some ammonia as well as water.

(c) Weighing as $Mg_2P_2O_7$. This is the classic method of weighing the precipitate, and the literature furnishes abundant proof of the fact that accurate results can be obtained. On the other hand, it is one of the hardest tasks that the beginner in analytical chemistry has to perform, because it is only by careful ignition that a pure, white residue can be obtained. If the precipitate is ignited too rapidly, a dark-colored ash is obtained. This is caused sometimes by incomplete combustion of the filter paper and sometimes by a reduction of the phosphate by the hot ammonia vapors that are being expelled. If the precipitation has taken place in the presence of sodium salts, sometimes a little sodium salt is absorbed by the precipitate and it melts during the ignition to form a coating which makes it difficult to burn all the carbon of the paper. Because of the difficulty involved and the fact that good results are possible, this determination as magnesium pyrophosphate furnishes good experience to the beginner.

$$2MgNH_4PO_4 \cdot 6H_2O \rightarrow 13H_2O + 2NH_3 + Mg_2P_2O_7$$
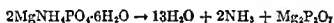
Use an ashless filter paper for filtering off the magnesium ammonium phosphate precipitate. After washing it with 1.5 N NH_4OH, exactly as described under (a), moisten it with a saturated solution of ammonium nitrate in 1.5 N ammonia, dry, ignite slowly and carefully, and weigh. The precipitate contains 36.21 per cent MgO.

The conversion of magnesium ammonium phosphate to magnesium pyrophosphate can also take place in a Gooch crucible. The crucible and its asbestos mat should be heated to about 800° and cooled in a desiccator before weighing it. After transferring the precipitate to the crucible and washing out all soluble salts, it should be dried at about 100° and then heated to about 800° for at least 15 minutes. If a muffle furnace is available this offers no difficulty. If the heating takes place over a free flame, a piece of platinum foil or the lid of a platinum crucible should be placed underneath the crucible so that the flame does not come into direct contact with the precipitate.

Alkalies. If it is desired to determine the alkalies the J. L. Smith method should be used (Chapter XII).

Loss on Ignition. Heat 0.5 g of the cement for 5 minutes in a platinum crucible over a low flame, then heat strongly for 15 minutes. The loss in weight usually represents $CO_2 + H_2O$.

Sulfuric Anhydride. Fuse, in an iron crucible, 0.5 g of cement with 2 g of sodium peroxide and an equal weight of sodium carbonate, protecting the contents of the crucible from the flame as directed on

p. 314. After the fusion, extract the soluble salts by treatment with hot water. Filter, make acid with hydrochloric acid, and evaporate to dryness on the steam table. Moisten the residue with 5 ml of 6 N hydrochloric acid, dilute with 200 ml of water, and filter. Wash thoroughly, and precipitate the sulfate in 400 ml of boiling solution by the addition of barium chloride (Chapter XI). Filter, ignite, and weigh. Report as percentage of SO_3.

POTASSIUM, K. At. Wt. 39.096

Forms: KCl, K_2SO_4, K_2PtCl_6, $KClO_4$, and $K_2NaCo(NO_2)_6$

1. Determination as Potassium Chloride

This compound is chosen for the determination of potassium when it is already present as such, or if the salt to be analyzed can be changed to chloride by evaporation with hydrochloric acid. If the potassium is present as sulfate it may be transformed to chloride by precipitation *of the sulfate* with barium chloride (see Chapter XII, "Silicate Analysis"); if it is present as the phosphate, the phosphoric acid may be precipitated as basic ferric phosphate (Vol. I); or, finally, if it is present as chromate the CrO_4^{--} ions may be reduced to chromic ions by evaporation with hydrochloric acid and alcohol and then precipitated by ammonia and filtered off.

In almost all these cases it is a question of separating the potassium chloride from the aqueous solution and usually of separating it from ammonium chloride as well.

Procedure. Evaporate the solution to dryness on the water bath in a platinum or thin *porcelain* dish, stirring frequently as soon as the salt begins to separate out in order to hasten the evaporation of the enclosed water. In spite of long-continued heating and continual stirring, however, it is not possible to expel all the water enclosed within the crystals; to accomplish this, heat the covered dish in a hot closet or drying oven for at least an hour at about 135°. Then remove the watch glass and heat carefully over a small flame until no more vapors are evolved, taking care not to heat too strongly because of the danger of volatilizing some potassium chloride. Usually there is a little carbon in the residue, due perhaps to a little pyridine in ammonia used in the analysis. Treat the residue with a little water and filter through a small filter into a weighed crucible or dish, preferably of platinum. Add a few drops of hydrochloric acid, carefully evaporate to dryness, and remove the last traces of moisture by drying and heating as before. Cool, weigh, and repeat the heating until a constant weight is obtained.

2. Determination of Potassium as Potassium Sulfate

This method is chosen when the potassium is already present in solution as the sulfate, or when it is in such a form that it can be readily changed to sulfate by evaporation with sulfuric acid; it is most fre-

quently used for determining the amount of potassium in combination with organic acids. No other cation except ammonium can be present.

Since the sulfate of potassium is much less volatile than the chloride, it is advisable to choose this method if no other metal is present. On the other hand, when it is necessary to separate potassium from sodium, it is preferable to have the potassium in the form of the chloride.

To determine the quantity of potassium in an organic salt, treat a known weight of the salt in a large, weighed crucible with a little concentrated sulfuric acid. Heat exactly as in igniting a moist precipitate (see p. 39), with the crucible in an inclined position and with the flame directed against the cover of the crucible. Thick, white fumes of sulfuric acid are soon evolved; as soon as these begin to diminish in quantity gradually move the flame toward the base of the crucible, and finally heat to dull redness until no more vapors are given off. The mass remaining in the crucible now consists of K_2SO_4 and $K_2S_2O_7$. The latter compound can be converted by stronger ignition into K_2SO_4 with loss of SO_3, but as this procedure involves a slight loss of potassium it is preferable to add a little solid ammonium carbonate, by means of which the excess of sulfuric acid is converted into ammonium sulfate, which is readily volatile and can be decomposed at a much lower temperature.

3. Determination of Potassium as Potassium Chloroplatinate

This and the following two methods are useful for determining potassium in the presence of sodium salts. Rubidium, cesium, and ammonium ions must be absent, as their chloroplatinates, perchlorates, and cobaltinitrites are insoluble under conditions which otherwise serve for the determination of potassium. The chloroplatinate method is generally considered to be the best way of determining potassium in the presence of sodium although the reagent is expensive. Although it is true that the platinum can be recovered quite easily from the precipitates and filtrates yet it takes considerable time to work up the residues into fresh reagent. The method is based upon the insolubility of potassium chloroplatinate in 80 per cent ethyl alcohol. Fresenius and Brinton[1] have shown that the solubility of potassium chloroplatinate is so slight that no allowance for dissolved K_2PtCl_6 is necessary if the volume of the filtrate and washings is kept at 50 to 75 ml. In the following procedure it is assumed that 0.25 g or less of alkali chlorides containing no ammonium, rubidium, or cesium salt is to be analyzed.

Procedure. Dissolve the weighed chlorides (0.25 g or less) with 5–10 ml of hot water in a small porcelain dish. Add enough chloroplatinic acid

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[1] *Z. anal. Chem.*, 50, 21 (1911); E. H. Archibald and his coworkers (*J. Am. Chem. Soc.*, 30, 755 [1908]) found that 100 ml of 80 per cent ethyl alcohol will dissolve K_2PtCl_6 equivalent to 2.0 mg K_2O, but the loss during an analysis will be considerably less than this value because the presence of H_2PtCl_6 and Na_2PtCl_6 in the filtrate will lower the solubility of the K_2PtCl_6.

to combine with all the alkali present, assuming, to be on the safe side, that the sample is all sodium chloride. Of the usual reagent, containing 10 g of dissolved platinum in 100 ml, 1.7 ml should be used for each 0.1 g of chloride. Enough water should be present to dissolve any precipitate of K_2PtCl_6 when the contents of the dish are heated on the water bath.[1]

Evaporate the solution on a water bath until the contents of the dish are sirupy and solidify on cooling. To the residue add 10 ml of 80 per cent ethyl alcohol (by volume) and break up the mass of crystals into a fine powder by means of a stirring rod or a platinum spatula. Decant the liquid through a filter moistened with alcohol, and repeat the treatment of the residue with 2-ml portions of alcohol until the filtrate runs through completely colorless and the salt remaining in the dish assumes a pure, gold-yellow color without any orange-colored particles ($Na_2PtCl_6 \cdot 6H_2O$).

Try not to get much if any of the precipitate upon the filter. Dry the dish and filter a few minutes to remove the alcohol, transfer the precipitate to a weighed crucible or very small dish, and wash out the original dish with several small portions of hot water poured through the above-mentioned filter. Evaporate to dryness on the steam bath, and heat for 30 minutes in an air bath at 135°, with the crucible or dish covered to avoid loss by decrepitation. Cool and weigh the K_2PtCl_6.

Notes. 1. When, as is commonly the case, the above procedure is used to determine potassium in the presence of sodium, it is advisable to add sufficient H_2PtCl_6 to convert both sodium and potassium to chloroplatinates. Sodium chloroplatinate is considerably more soluble in alcohol then sodium chloride   To lessen the requirement of chloroplatinic acid, Smith and Shead (*J. Am Chem. Soc.*, **54**, 1722 [1932]) recommend first adding perchloric acid to the aqueous solution of sodium and potassium ....). The residue
.... ore than enough
.... it is not neces-
sary to form Na_2PtCl_6.

This procedure is useful for determining small quantities of potassium in the presence of considerable sodium. (Cf. G. L. Smith and J. L. Gring, *J. Am. Chem. Soc.*, **55**, 3957 [1933]).

2. Instead of weighing the K_2PtCl_6 it has been recommended that it be heated strongly in a stream of hydrogen. The reaction

$$K_2PtCl_6 + 2H_2 = 4HCl + Pt + 2KCl$$
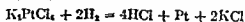
takes place, and the KCl content can be calculated by determining the quantity of HCl evolved, the weight of the residual mixture of KCl + Pt, the weight of the KCl obtained by evaporating the aqueous extract of the residue, or by weighing the Pt alone after dissolving out the KCl with water. Values based upon such determina-

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[1] A convenient bath is obtained by placing the dish on a beaker half filled with water, which is kept just below the boiling point by a flame beneath the beaker or by a hot plate.

tions are usually a little low. Hicks, *J. Ind. Eng. Chem.*, 5, 650 (1913), recommends dissolving the K_2PtCl_6 in hot water, adding 4 ml of concentrated hydrochloric acid and 0.5 g of magnesium wire for each 0.2 g of K. When the action subsides a little more acid is added to dissolve the magnesium and the residual platinum is filtered off into a filtering crucible, washed with hot water, heated strongly, and weighed.

3 For determining very small quantities of potassium, Cameron and Failyer, *J. Am. Chem. Soc*, 25, 1063 (1903), recommend a colorimetric method based on the formation of red K_2PtI_6. Isolate the potassium as K_2PtCl_6, as in the procedure recommended above, but instead of weighing it dissolve the washed precipitate in a little hot water and 1 drop of concentrated hydrochloric acid. Add an excess of strong potassium iodide solution (at least 5 times as much as is theoretically necessary), wait 4 hours, and then compare the red color with that obtained similarly with known quantities of potassium.

4. L. A. Hill, *J. Am. Chem. Soc.*, 25, 990 (1903), has recommended a colorimetric method which is based upon the yellow color formed when a solution containing a little K_2PtCl_6 is reduced with stannous chloride. With this method be determined from 1 to 21 parts of K_2O per million parts of water, and the values were within 10 per cent of the truth.

4. Determination of Potassium as Perchlorate, $KClO_4$[1]

Principle. The perchlorates of sodium and lithium are soluble in 97 per cent alcohol but the perchlorates of potassium, rubidium, and cesium are practically insoluble. Usually the quantities of rubidium and cesium present are negligible.

Ammonium salts and sulfates must not be present on account of the difficult solubility of ammonium perchlorate and of sodium sulfate in alcohol, but a little phosphate does no harm, as both sodium perchlorate and phosphoric acid are soluble in alcohol.

Many experiments by the agricultural chemists of the United States show that the method is nearly, if not quite, as accurate as the chloroplatinate method. It requires a little more attention to details, but the reagent is much less expensive.

In the analysis of fertilizers, the Association of Official Agricultural Chemists recommends placing 2.5 g of sample on a 12.5-cm filter paper in a funnel and dissolving the soluble salts by treating with small portions of hot water until about 200 ml of filtrate is obtained. Then 5 ml of concentrated hydrochloric acid is added and the sulfate precipitated by barium chloride. The solution is diluted to exactly 250 ml in a calibrated flask, and, after mixing thoroughly, a little of the solution is filtered through a dry filter and exactly 50 ml of filtrate taken for the rest of the analysis.

By taking a fairly large portion for analysis and then using an aliquot part, a more representative analysis is obtained if the sample is not perfectly uniform. It is assumed that the actual volume of precipitate can be neglected, and no attention is

[1] Schlösing-Wense, *Z. angew. Chem.*, 4, 691; 5, 233; 6, 68; *Landw. Ver. Sta.*, 59, 313; 67, 145; *J. Am. Chem. Soc.*, 36, 2085. Cf. also *U. S. Chem. Bull.* 152; Baxter and Kobayashi, *J. Am. Chem. Soc.*, 39, 249 (1917); 42, 735 (1920); Davis, *J. Agr. Sci.*, 5, 52 (1912); Gooch and Blake, *Am. J. Sci.*, 44, 381 (1917); T. D. Jarrell, *J Assoc. Official Agri. Chem.*, 4, 76–77 (1920–21); H. H. Willard, *J. Am. Chem. Soc*, 34, 1480 (1912); H. H. Willard and G. F. Smith, *ibid.*, 44, 2816 (1922); 45, 293 (1923); G. F. Smith, *ibid.*, 47, 762 (1925); G. F. Smith and J. F. Ross, *ibid*, 47, 774 and 1025 (1925).

paid to adsorption of solute by the precipitate or by the filter paper. Such effects must be considered when pure substances are to be analyzed with the greatest possible accuracy, but when the weight of precipitate is small or the percentage of desired constituent low it is permissible to neglect the volume of precipitate and adsorption, especially as the errors tend to compensate one another.

SOLUBILITY OF ALKALI PERCHLORATES

(100 ml of solvent, dissolve at 25°)

Salt	Water g/100 ml	CH_3OH g/100 ml	C_2H_5OH g/100 ml	n-Butyl Alcohol g/100 ml	Ethyl Acetate g/100 ml
$NaClO_4$.	113 9	35.9	11.13	1.50	8.43
$LiClO_4$	47.42	89.4	79.4	49.3	63.4
NH_4ClO_4....	21 91	5.27	1.49	0.014	0.029
$KClO_4$.....	2 04	0.0830	0 0094	0.0036	0.0013
$RbClO_4$ ..	1.33	0.0472	0 0071	0.0016	0.0014
$CsClO_4$...	1 96	0.0734	0 0086	0 0048	0.001

Procedure. If the solution to be analyzed contains sulfate, it is advisable to remove it. To about 70 ml of solution (containing not more than 0.5 g of potassium salt) add 1 ml of concentrated hydrochloric acid, heat to a gentle boil, and add hot 0.5 N barium chloride solution drop by drop until no further precipitation occurs. Wait 15 minutes; filter off the barium sulfate, and wash it with hot water.

If ammonium salts are present, evaporate to dryness in a porcelain dish and ignite carefully till all ammonium salts are decomposed. Cool, rinse down the sides of the dish with a little water, again evaporate, and ignite at a temperature below redness. Dissolve the residue in about 20 ml of water and transfer to a 150-ml Pyrex beaker.

Method 1

Two methods for carrying out the perchlorate separation of potassium (rubidium and cesium) from sodium (and lithium) will be given.

The first method depends upon the use of ethyl alcohol containing a little perchloric acid to make the perchlorate of potassium practically insoluble. This is the common method H. H Willard, however, prefers to make use of normal[1] butyl alcohol, and many chemists follow this procedure.[2]

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[1] Normal butyl alcohol is $CH_3CH_2CH_2CH_2OH$. The word *normal* is used to distinguish it from its isomers $(CH_3)_2CH_2CH_2OH$ (called isobutyl alcohol), $CH_3CH_2CHOHCH_3$ (called secondary butyl alcohol), and $(CH_3)_3COH$ (called tertiary butyl alcohol) To show that the word *normal* does not refer to normal concentration, the small letter n will be used in the directions, whereas N will signify normal in the sense of concentration.

[2] Cf Hillebrand and Lundell, *Applied Inorganic Analysis*

Add 5 ml of perchloric acid, d 1.12, containing 20 per cent $HClO_4$, and evaporate carefully till salts separate. Add 10 ml of hot water, 5 ml more of perchloric acid, and again evaporate on a water bath and finally on a sand bath. If dense fumes of perchloric acid are not evolved, repeat the addition of water and perchloric acid until dense fumes are obtained by evaporation. Cool to below room temperature and add 20 ml of 97 per cent alcohol containing 0.2 per cent of perchloric acid and saturated with potassium perchlorate.[1] Crush the precipitated $KClO_4$ with the end of a stirring rod and allow to stand for 30 minutes, preferably with the dish resting in ice water. Filter through a Gooch or Munroe crucible that has been dried at 120–130° and weighed.

If only a small precipitate is obtained, it is safe to wash and weigh it at once without purification provided that no considerable quantity of other salt is present in the alcoholic solution. Unless the absence of much sodium or other salt is assured, decant the solution through the filter and wash the crystals 3 times with small portions of alcohol containing 0.2 per cent of perchloric acid. Then dissolve the crystals in a little hot water, add 1 ml of perchloric acid, evaporate, and treat as before. Transfer the pure potassium perchlorate to the weighed filtering crucible, and wash with small portions of cold alcohol[2] which is saturated with $KClO_4$ besides containing 0.2 per cent of $HClO_4$. Dry at 130° for an hour and weigh.

Method 2

In this procedure the alkali perchlorates are digested with a mixture of n-butyl alcohol and ethyl acetate in which the perchlorate of potassium (rubidium and cesium) is insoluble. After filtering off the potassium perchlorate, the sodium can be precipitated as sodium chloride by adding a solution of hydrogen chloride gas dissolved in butyl alcohol. Then, if lithium is present, it can be weighed as sulfate after evaporating the filtrate from the sodium chloride precipitation.

To the solution of chlorides add 2 or 3 times as much of 9 N perchloric acid as is theoretically necessary to convert the chlorides to perchlo-

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[1] One hundred milliliters of the alcohol containing perchloric acid will dissolve 2.8 mg of $KClO_4$. If considerable $NaClO_4$ is present it tends to salt out a little $KClO_4$ from the saturated alcoholic solution. When considerable sodium salt is present, therefore, it is advisable to wash the first precipitate with a little alcohol containing no potassium perchlorate, dissolve the precipitate in a little water, and repeat the precipitation. The small quantity of sodium salt adhering to the partially washed $KClO_4$ precipitate will do no harm the second time. (Cf. Davis, *J. Agr. Sci.*, 5, 52, 512; Gooch and Blake, *Am. J. Sci.*, 44, 381; Baxter and Kobayashi, *J. Am. Chem. Soc.*, 42, 725.)

[2] Baxter and Kobayashi have shown that it is advisable to cool the wash alcohol to 0° and to keep the volume of the washings as small as possible.

rates (not less than 1 ml in any case). Evaporate to dryness on the hot plate, at a temperature not exceeding 350°, and expel any acid condensed on the side walls of the beaker by playing a free flame along the outside. Cool, wash down the sides of the beaker with 3 to 5 ml of hot water, and again evaporate to dryness on the hot plate. Cool; add 10 to 20 ml of a mixture of equal parts by volume of *n*-butyl alcohol and ethyl acetate. Digest on the steam bath[1] for 2 or 3 minutes and then cool to room temperature.

Decant the liquid through a previously ignited and weighed filtering crucible and wash the precipitate 3 times by decantation with 5-ml portions of the alcohol-acetate mixture. Reserve the filtrate and washings if it is desired to make a direct determination of sodium.

Dissolve the residue in the crucible with a very little hot water, catching the solution in the original beaker. Again evaporate to dryness. Add 10 ml of the butyl alcohol-acetate mixture; digest and cool as before. Filter through the original crucible, which has been dried meanwhile. Transfer the precipitate to the crucible and wash 10 to 15 times with less than 1-ml portions of the alcohol-acetate mixture. Dry the beaker and brush any particles of potassium perchlorate into the crucible. Dry an hour at 110° and 15 minutes at 350°. Cool and weigh as $KClO_4$.

Remark. The precipitation of potassium as perchlorate can be accomplished in the presence of most other cations except ammonium, rubidium, and cesium. The precipitate should be easily soluble in hot water. In the analysis of fertilizers it is often recommended to dissolve the precipitate in hot water, dry, and weigh again to see if any other insoluble substance was present with the precipitated potassium perchlorate

5. Determination of Potassium as Cobaltinitrite, $K_2NaCo(NO_2)_6$

Sodium cobaltinitrite is probably the most sensitive precipitant of potassium ions in aqueous solution. Bülmann[2] was able to detect 0 0009 mg. of potassium in the presence of 4000 equivalents of sodium. Since de Koninck[3] recommended the reaction in 1881, the quantitative determination of potassium as cobaltinitrite has been studied by many chemists, most of whom have been able to get satisfactory results.

Produced under ideal conditions, the precipitate, formed in dilute acetic acid solution with a considerable excess of the reagent, corresponds to the formula $K_2NaCo(NO_2)_6$, with 17.93 per cent of potassium, equivalent to 21.59 per cent K_2O. From saturated NaCl solutions, the precipitate has the formula $K_2Na_2[Co(NO_2)_6]_2$.

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[1] Be careful not to use a free flame because if the combustible vapors catch fire a dangerous explosion will result.

[2] *Z. anal Chem.*, 39, 284 (1900).

[3] *Ibid*, 20, 390 (1881).

The reagent sodium cobaltinitrite is not very stable, and the composition of the precipitate varies somewhat when produced under different conditions. For this reason, Vurtheim and others have recommended the use of empirical factors, and the Association of Official Agricultural Chemists has abandoned the method although many of its cooperating chemists obtained excellent results.

The precipitate can be filtered, dried at 110°, and weighed without decomposition; it may be dissolved and the cobalt determined electrolytically;[1] the nitrite may be determined volumetrically;[2] or the volume of the precipitate may be measured in a graduated centrifuge tube.

Reagent. Dissolve 28.6 g of cobaltous nitrate crystals and 50 ml of glacial acetic acid in enough water to make 500 ml of solution. Dissolve 180 g of sodium nitrite in 500 ml of water. Keep these two solutions separate until the day before the analysis is to be made, then mix equal volumes, shake or stir well, allow to stand over night in a glass-stoppered bottle, and filter just before using.

Procedure.

The potassium solution should contain the equivalent of 0.25 g KCl, or less, in a volume of 25 ml. For this weight of potassium salt use 40 ml of the filtered reagent. For smaller quantities of potassium, use less solution and less reagent but never less than 10 ml of either. Shake the mixture vigorously for several minutes, or, better still, stir mechanically for 30 minutes and allow to stand over night. Filter through a Gooch crucible; wash with 10 per cent acetic acid until the filtrate comes through colorless and then with 95 per cent alcohol. Dry at 110° for 2 hours.

Remark.

The presence of sodium salts in considerable excess does no harm. Most other cations can be removed by adding sodium carbonate solution. Ammonium salts should be removed, when present, by evaporating to dryness and gently igniting the residue. In fertilizer analysis, a fairly large sample should be taken and an aliquot part used for the potassium determination after the removal of ammonium salts and precipitation of other cations with sodium carbonate. Clerfeyt tested the method and obtained satisfactory results with materials containing from 5 to 62 per cent of K_2O. In most cases the agreement between the cobaltinitrite method and the chloroplatinate method was nearly, if not quite, as good as is usually obtained with duplicate analyses by the chloroplatinate method. When these directions are followed, the method appears to be rapid, exact, and economical.

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[1] Dissolve the precipitate in dilute hydrochloric acid, boil to decompose the nitrite, and carry out the electrolysis as described under "Cobalt."

[2] Boil the washed precipitate with dilute sodium hydroxide, filter off the cobaltic hydroxide, make the filtrate acid, and titrate with permanganate as described in Chapter XV, "Analysis of Nitrous Acid"; 1 ml of 0.1 N $KMnO_4 = 0.000785$ g K_2O. Another method — Wash the precipitate into a measured volume of hot permanganate solution diluted with 10 times as much water. After 5–6 minutes make acid with 5 N H_2SO_4 and titrate the excess permanganate with standard oxalate solution. In this case, 1 ml 0.1 N $KMnO_4 = 0.000856$ g K_2O.

6. Determination of Potassium in a Silicate[1]

Most silicates are decomposed by treatment with hydrofluoric acid in the presence of a dehydrating agent such as sulfuric acid, concentrated hydrochloric acid, or perchloric acid. The perchlorates of all the common cations, except those of potassium and ammonium, are soluble in alcohol.

Procedure. To about 0.3 g of silicate in a platinum crucible add 1.5 ml of $2 N$ HClO$_4$ and 3–4 ml of 48 per cent HF. Evaporate to dense fumes of HClO$_4$, heating at a low temperature on a sand bath in a larger crucible or in a wire gauze chamber made by bending some fairly fine-meshed copper or bronze gauze and inserting a triangle to hold the crucible. Cool, add water to fill about two-thirds of the crucible, heat just to boiling, filter, and wash thoroughly with hot water. Evaporate the filtrate till fumes of HClO$_4$ are again obtained. Cool and add 25 ml of 97 per cent alcohol. Break up the residue with a stirring rod,[2] and filter through a Gooch crucible. Wash the precipitate with 1 per cent perchloric acid in alcohol. Transfer the washed precipitate and the asbestos mat to a filter and wash thoroughly with hot water to dissolve the KClO$_4$. Some insoluble salts are usually left on the filter. To the filtrate add 1 ml more of perchloric acid, evaporate to fumes, and treat with alcohol when cold. Usually the precipitate is now pure KClO$_4$. Filter, wash with 1 per cent perchloric acid in alcohol, dry for 1 hour at 110°, and weigh as KClO$_4$.

SODIUM, Na.   At. Wt. 22.997

Forms: NaCl, Na$_2$SO$_4$, NaZn(UO$_2$)$_3$(C$_2$H$_3$O$_2$)$_9$·6H$_2$O,
NaMg(UO$_2$)$_3$(C$_2$H$_3$O$_2$)$_9$·6½H$_2$O

1. Determination as Chloride, NaCl

The procedure is the same as described under " Potassium " (p. 269), but there is not so much danger of loss by volatilization. The chief difficulty lies in avoiding loss by spattering when the crystals containing water break by the pressure exerted by the steam formed inside the crystals. This can be avoided by heating the residue from the evaporation in a hot closet at 120–130° before attempting to heat the dish containing the chloride over a free flame to drive off any ammonium salts that may be present. Dishes of platinum or of fused silica are suitable

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[1] J. J. Morgan, *J. Ind. Eng. Chem.*, **13**, 225 (1921); M. M. Green, *ibid.*, **15**, 163 (1923)

[2] This is important. If the crystals are not fine, it will be necessary to repeat the following purification process.

for the determination, and evaporation to dryness is accomplished conveniently by placing the disb on a beaker half full of water kept gently boiling.

2. Determination as Sulfate, Na₂SO₄

The procedure is the same as described under "Potassium" (p. 269). The sulfate is heavier than an equivalent weight of the chloride, and it can be heated to a much higher temperature without fear of loss. The sulfate is easily obtained by evaporation with sulfuric acid provided that no phosphoric, boric, arsenic, silicic, tungstic, or other non-volatile acid is present. The last of the sulfuric acid is retained tenaciously and requires treatment with ammonium carbonate for its complete expulsion. The sulfate is slightly hygroscopic.

3. Determination as Sodium Uranyl Zinc Acetate

Principle. The solubility of the triple acetate of sodium, uranyl, and zinc in pure water is fairly great; 5.85 g of the salt dissolves in 100 ml of water. Under proper conditions, however, as little as 0.013 mg of sodium can be detected by the formation of the yellow precipitate or turbidity, and the test is about five times more sensitive if the reaction takes place under ultraviolet light and the precipitate is recognized by its bright greenish-yellow fluorescence; the reagent itself shows no fluorescence. The procedure to be described is excellent for the determination of 0.5 to 50 mg of sodium in the presence of not more than 2 mg of lithium or 0.2 g of potassium. The precipitate is too bulky to be used for larger quantities.

Reagents. *Uranyl Zinc Acetate.* Mix equal volumes of solutions (a) and (b), allow to stand 24 hours to remove any precipitate formed from impurity in the reagents, filter, and preserve in a Pyrex bottle.

Solution (a). Mix 10 g of $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$, 6 ml of 30 per cent acetic acid, and 50 ml of water; heat until the solid dissolves.

Solution (b). Mix 30 g of $Zn(C_2H_3O_2)_2 \cdot 3H_2O$, 3 ml of 30 per cent acetic acid, and 50 ml of water; heat until the solid is dissolved.

Besides these, ether or acetone and some ethyl alcohol which has been shaken with pure sodium uranyl zinc acetate at room temperature until saturated with the salt are required.

Procedure. To about 5 ml of aqueous solution containing not more than 8 mg of sodium or 0.1 g of potassium add 10 ml of uranyl zinc acetate solution, mix, and allow to stand for 30–60 minutes. Filter through a filtering crucible, drain dry, and wash the precipitating vessel and crucible with five to eight 2-ml portions of the reagent, always draining out all the liquid before adding another portion. Now wash 5 times with 2-ml portions of 95 per cent alcohol saturated with the precipitate and then with five 2-ml portions of ether or acetone. Finally draw air through the crucible for 5 minutes, wipe off any condensed moisture on the outside, cool in the balance case for 10 minutes, and weigh. The

precipitate contains 1.495 per cent sodium. The results are said to be within 0.5 per cent of the actual content.

Remarks. 1. Instead of weighing the precipitate, the uranium content can be determined by titration with standard disodium hydrogen phosphate (35 g $Na_2HPO_4 \cdot 12H_2O$ per liter) using potassium ferrocyanide test paper (filter paper dipped in 10 per cent potassium ferrocyanide solution and dried) as an outside indicator. Moisten the precipitate with 2–2.5 ml of glacial acetic acid and dissolve it in 40–50 ml of hot water. Titrate at 90° with the phosphate solution until a drop of the clear solution, free from any uranyl phosphate precipitate, will not give a brown color when placed on a piece of the test paper. The precipitate formed is UO_2HPO_4.

2. If more than 2 mg of lithium is present it should be removed, and this is best accomplished by precipitation as fluoride The excess fluoride must then be removed by evaporating in platinum with hydrochloric acid. This is accomplished as follows:[1]

To not more than 0.1 g of the salt add 10 ml of water and 5 ml of 95 per cent alcohol. After the salt has dissolved, add 5 ml of 10 per cent ammonium fluoride solution to which a little ammonium hydroxide has been added to decompose any fluosilicate which is likely to be present in the reagent. After standing for at least 20 hours, filter off the precipitate of Li_2F_2 and wash it 5 times with 2-ml portions of 50 per cent alcohol containing 0.5 per cent of ammoniacal ammonium fluoride. Evaporate the filtrate to dryness in a platinum dish and moisten the residue with 5 ml of concentrated hydrochloric acid. Evaporate to dryness and repeat this treatment with hydrochloric acid twice more, after which it can be assumed that the final, dry residue contains neither lithium nor fluoride.

3. If more than 0.2 g of potassium is present, the greater part should be removed by treatment with perchlorate. This treatment also serves to remove rubidium and cesium which, however, cause less interference. To determine sodium in commercial potassium chloride, dissolve 1 g of the salt in 5 ml of water and add a hot solution of 2 g of NH_4ClO_4 in 3 ml of water. Cool to room temperature, filter, and wash the precipitate 5 times with 2-ml portions of 95 per cent alcohol. Evaporate to dryness, heat strongly, and determine sodium in the residue.

4. The presence of phosphate or arsenate interferes with the determination of sodium as complex acetate. They should be removed by treatment with "magnesia mixture." Evaporate the filtrate to dryness, heat to expel ammonium salts, treat the residue with hot water, filter, and use the filtrate for the sodium determination.

4. Determination as Sodium Magnesium Uranyl Acetate

The precipitate contains 1.527 per cent of sodium. It serves for the determination of sodium in quantities of 0.5 to 50 mg but is so bulky that it is unsuitable for larger quantities. The presence of more than 2 mg of lithium or 0.2 g of potassium causes interference and high results; small quantities of rubidium, cesium, ammonium, or alkaline earths do no harm Phosphates and arsenates must be absent.

Reagent. Dissolve, separately, 85 g of $UO_2(C_2H_3O_2)_2 \cdot 3H_2O$ and 500 g of $Mg(C_2H_3O_2)_2 \cdot 4H_2O$ in 1 l of normal acetic acid. Heat each solution to about 70°, mix at this temperature, and allow to cool to 20°. Keep at this temperature for at least an hour and filter. In this way 2 l of reagent is obtained, of which 100 ml

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[1] Cf. Barber and Kolthoff, *J. Am. Chem. Soc.*, **51**, 3233 (1929).

should be used when the quantity of sodium present is 10 mg or less and in all cases 10 ml is desirable for each milligram of sodium likely to be present.

Procedure. Concentrate the aqueous solution, preferably of chlorides, to 5 ml, or less, if there is no separation of solid salt. Add 10 ml of reagent for each milligram of probable sodium content, with not less than 100 ml in any case, place in a beaker of water at 20°, and stir vigorously for 30–35 minutes. Filter into a weighed Gooch, Munroe, or glass filtering crucible and wash with 5-ml portions of 95 per cent ethyl alcohol which has been saturated with solid uranyl-magnesium-sodium acetate. (If ordinary 95 per cent ethyl alcohol is used, assume that each 5 ml dissolves 1 mg of the precipitate.) Dry at 105° for 35 minutes and weigh.

Separation of Sodium and Potassium

The separation of the alkali cations from one another is somewhat a problem because most salts of the alkalies are fairly soluble in water. The elements lithium, rubidium, and cesium are not present in common minerals to an appreciable extent so that ordinarily the chemist is concerned chiefly with the determination of only sodium and potassium. In general, it may be stated that the compounds of rubidium and cesium resemble those of potassium, and when a potassium salt is less soluble than the corresponding sodium salt, the rubidium and cesium salts will be still less soluble. The relationship between increasing atomic weight and solubility helps one to remember the relative solubilities.

The salts of potassium which are distinctly less soluble than the corresponding sodium salts, and which have been proposed for the identification and determination of potassium ions, are the chloroplatinate, K_2PtCl_6, the perchlorate, $KClO_4$, the cobaltinitrite, $K_3NaCo(NO_2)_6$, the acid tartrate (cream of tartar), $KHC_4H_4O_6$, and the double sulfate with zirconium, $2ZrO_2 \cdot K_2O \cdot (SO_3)_5$. The first of these compounds, potassium chloroplatinate, is practically insoluble in alcohol whereas the anhydrous sodium chloroplatinate dissolves in alcohol. By adding sufficient chloroplatinic acid, H_2PtCl_6, to combine with both the sodium and potassium and evaporating to dryness, it is possible to convert a mixture of sodium and potassium chlorides into one of chloroplatinates and then the sodium chloroplatinate can be dissolved in alcohol leaving behind the potassium chloroplatinate which can be dried and weighed (cf. p. 271). This method is perhaps the oldest and best known for separating sodium and potassium. It is still widely used but is costly, owing to the high price of platinum and the time required to recover this element from the precipitates and mother liquors. Moreover, the composition of the precipitate does not always correspond exactly to the formula K_2PtCl_6. The method is not so accurate as is sometimes assumed.

The separation by means of sodium cobaltinitrite reagent has received considerable attention in the literature (cf. p. 275). The precipitate of potassium cobaltinitrite is much less soluble than potassium chloroplatinate; it can be weighed as $K_3NaCo(NO_2)_6$, the cobalt content can be determined electrolytically, or the nitrite content by oxidation with permanganate. The cobaltinitrite method for separating potassium and sodium was recommended by de Koninck,[1] and since then many

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[1] *Z. anal. Chem.*, **20**, 390 (1881).

chemists have testified to its usefulness. The reagent, however, is not very stable, and the composition of the precipitate is not always the same.

The precipitation of potassium by zirconium sulfate in a concentrated, neutral, aqueous solution has been recommended; it furnishes a means of separating sodium and potassium which is a promising one. According to Reed and Withrow[1] the precipitation of potassium can take place in the presence of sodium, ammonium, lithium, rubidium, and cesium ions, but this statement is contradicted by Yajnik and Tandon,[2] who have found it possible to precipitate rubidium and cesium quantitatively by means of zirconium sulfate in a neutral solution.

A method often used for estimating the sodium and potassium content in a weighed portion of their chlorides is to determine the chloride content by titration with silver nitrate solution or by adding a measured volume of silver solution and titrating the excess silver with thiocyanate solution (Chapter XVII). This method is rapid but not altogether satisfactory because the chloride content of potassium chloride does not differ sufficiently from that of sodium chloride; any error in the titration is multiplied nearly eightfold in estimating the composition of the original mixture.

Probably the most reliable method for analyzing a mixture of sodium and potassium chlorides is the modification of the perchlorate method which has been worked out by H. H. Willard and his associates (cf. p 272). The sodium content can be determined from the original weight of the NaCl + KCl after deducting a weight of potassium chloride equivalent to that of the potassium perchlorate found, or the filtrate from the potassium perchlorate precipitate can be evaporated to remove the ethyl acetate and the sodium precipitated as chloride by adding a solution of hydrogen chloride in butyl alcohol.

To determine the sodium, evaporate the combined filtrates and washings from the potassium perchlorate precipitation till the volume is not over 20 ml at the most and all the ethyl acetate has been removed. Heat to 80 to 90°, and add dropwise, with stirring, 2 ml of a 20 per cent solution of hydrogen chloride in n-butyl alcohol (prepared by passing dry hydrogen chloride into 200 ml of butyl alcohol for 2 hours; the density of the solution is 0.905). Then add 6 ml more of the HCl-alcohol solution, cool to room temperature, filter off the precipitated sodium chloride, and wash 8 or 10 times with 1-ml portions of 6 to 7 per cent solution of hydrogen chloride in butyl alcohol. Dry 15 minutes at 110° and then for 5 minutes at 600°. Cool and weigh as NaCl or dissolve the salt in water and titrate the chloride (see Chapter XVII).

LITHIUM, Li.   At. Wt. 6.94

Forms: Li₂SO₄ and LiCl

The determination of lithium in the form of the above salts is carried out in practically the same way as that of potassium. It should be mentioned, however, that on evaporating a lithium salt with concen-

[1] J. Am. Chem. Soc., 51, 1062 (1929).

[2] J. Indian Chem. Soc., 7, 287–296 (1930).

trated sulfuric acid the acid salt, $LiHSO_4$, is formed, which on gentle ignition (even without the addition of ammonium carbonate) is changed to difficultly volatile Li_2SO_4.

Since lithium chloride is a very hygroscopic salt, it is necessary to weigh it out of contact with moist air. To accomplish this, place the platinum crucible, after being gently ignited, together with a glass-stoppered weighing beaker in a desiccator which is provided with a calcium chloride tube. After they have assumed the temperature of the room, quickly place the crucible within the beaker, and stopper. Allow the weighing beaker to stand for 20 minutes in the balance case and then weigh. Place the salt in the crucible and repeat the above process.

Determination of Lithium in the Presence of Sodium and Potassium

Two methods for determining the lithium content of a mixture of the chlorides of sodium, potassium, and lithium have already been pointed out (pp. 274, 279). In one, the potassium was removed first as $KClO_4$, then the sodium as $NaCl$, and the lithium was determined in the filtrate as Li_2SO_4. In the other method, the lithium was removed first as Li_2F_2. Most methods for separating lithium from the other alkalies are based upon the fact that the solubility of lithium chloride in various solvents is usually greater than the solubilities of the chlorides of sodium and potassium.

The method of Gooch[1] depends upon the fact that lithium chloride is soluble in anhydrous amyl alcohol. Rammelsberg's[2] method is based on the solubility of anhydrous lithium chloride in a mixture of equal parts alcohol and ether. Kahlenberg and Krauskopf's[3] method depends upon the fact that lithium chloride is soluble in pyridine containing less than 3 per cent water. Brown and Reedy[4] used dry acetone, and Sinka[5] used diethylene oxide (also called dioxan, CH_2 CH_2).
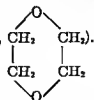
Gooch's method is the oldest and best known, but the pyridine method of Kahlenberg and Krauskopf does not require correction for the solubility of lithium chloride; both methods suffer because of the odor and physiological effects of the reagents. The procedure of Brown and Reedy and that of Sinka are easier to carry out than the other methods; judging from the published data, all the methods are about equally accurate.

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[1] *Proc. Am. Acad. Arts Sci.*, 22 [N. S 14], 177 (1886).

[2] *Pogg. Ann.*, 66, 79 (1845). Cf. S. Palkin, *J. Am. Chem. Soc.*, 38, 2326 (1916).

[3] *J. Am. Chem. Soc.*, 30, 1104 (1908).

[4] *Ind. Eng. Chem., Anal. Ed.*, 2, 304 (1930).

[5] *Z. anal. Chem.*, 80, 430 (1930).

(a) Gooch's Method

Principle. Anhydrous LiCl is soluble in anhydrous amyl alcohol (10 ml of cold amyl alcohol dissolves 0.66 g LiCl) while KCl and NaCl are difficultly soluble in this liquid (10 ml dissolves 0.3 mg NaCl and 0.4 mg KCl).

Procedure. Place the concentrated solution, containing not more than 0.2 g LiCl, in a 50-ml Erlenmeyer flask, add 5–6 ml of amyl alcohol (boiling point 132°), and carefully heat on an asbestos plate. The aqueous solution at the bottom of the beaker soon begins to boil and the water vapor escapes through the upper layer of amyl alcohol. To prevent loss by bumping at this point, it is well to pass air through the liquid during the boiling; the water evaporates more quickly and without bumping. As soon as all the water has been boiled off, the chlorides of sodium and potassium separate out and nearly all the lithium chloride dissolves in the alcoholic solution. During the evaporation of the aqueous LiCl solution, however, some LiOH is formed by hydrolysis, and this compound is insoluble in amyl alcohol. To dissolve it, add 2–3 drops of concentrated hydrochloric acid, boil 2 or 3 minutes, and filter while still warm through a small asbestos filter. The insoluble residue is composed of sodium and potassium chlorides. Wash it with hot amyl alcohol, which has been boiled. Evaporate the filtrate to dryness, and dissolve the residue in a little water and a little dilute sulfuric acid. Filter off the carbonaceous residue into a weighed platinum crucible, evaporate as far as possible on the water bath, remove the excess of sulfuric acid by gentle heating over a flame (the crucible being placed in an inclined position), and then weigh. The lithium sulfate thus obtained will contain small quantities of potassium and sodium sulfates if the corresponding cations are present. To correct for these impurities subtract 0.00041 g for every 10 ml of the filtrate (exclusive of the alcohol used in washing the residue) if only sodium chloride is present, 0.00051 if only potassium chloride is present, and 0.00092 if both sodium and potassium chlorides are present.

If only 10–20 mg of lithium chloride was present in the original salt mixture, then, after filtering and washing with amyl alcohol, dissolve the residue in a little water, repeat the above treatment, and determine the lithium in the combined filtrates.

(b) Rammelsberg's Method (Modified by S. Palkin)

Principle. Anhydrous lithium chloride is soluble in a mixture of alcohol and ether, whereas the chlorides of sodium and potassium are practically insoluble.

Procedure. Dissolve the chlorides in a little water (not over 1.5 ml for 0.5 g of salts) in a tall beaker. Add 1 drop of concentrated hydrochloric acid to react with any LiOH that may be formed by hydrolysis, and introduce gradually, while rotating the contents of the beaker, 20 ml of absolute alcohol; drop the alcohol into the center of the solution and not down the sides of the beaker. This should cause the deposition of granular sodium and potassium chlorides. While still rotating the beaker, add 60 ml of ether and allow the mixture to stand 5 minutes or until the precipitate has settled well and the supernatant liquid is nearly clear. Filter through a filtering crucible, wash with a mixture of 1 part alcohol and 4 or 5 parts ether and set the crucible aside. Evaporate the filtrate in an Erlenmeyer flask on the steam bath. Take up the residue in 10 ml of absolute alcohol and heat if necessary so that practically everything dissolves. If a film remains, remove it by scrubbing. Rotate the flask while adding 50 ml of ether, add 1 ml concentrated hydrochloric acid, rotate, and let stand half an hour with frequent rotating. Filter through the same crucible that was used before, wash with ether-alcohol, dry, ignite gently, and weigh the residual chlorides of sodium and potassium.

To determine the lithium, carefully evaporate the filtrate on the steam bath, take up the residue in a little water, transfer to a weighed platinum or quartz dish, add a little sulfuric acid, evaporate to dryness, heat to about 600°, and weigh as $LiSO_4$.

(c) Separation by Pyridine, Method of Kahlenberg and Krauskopf as Modified by Mellor

Evaporate the solution of 2 g or less of the chlorides to dryness, add 2 drops of concentrated hydrochloric acid, and again evaporate. Digest the residue with 25 ml of boiling anhydrous pyridine for 5 to 10 minutes. To prepare a suitable reagent, dry commercial pyridine over potassium hydroxide and redistil; use the fraction that boils between 114° and 116°.

After adding the pyridine, break up any large masses of salt with the end of a stirring rod. Let settle, filter through a small filter, and wash with 5 ml of hot pyridine; catch the filtrate in an Erlenmeyer flask. Dissolve the residual sodium and potassium chlorides in a little water containing a drop of hydrochloric acid, again evaporate, and repeat the above treatment to remove any residual lithium chloride. With large quantities of sodium and potassium chlorides and very little lithium chloride, evaporate and extract with pyridine once more. Evaporate off the pyridine from the filtrate, add a little sulfuric acid, transfer to a

weighed platinum or silica dish, evaporate to dryness, dry at 110–120°, and carefully heat until the mass fuses slightly. Cover the dish, to prevent loss by spattering as the melt cools, and weigh as Li_2SO_4.

(d) Method of Brown and Reedy

Evaporate the solution of chlorides to dryness in a platinum or silica dish. Dry for one hour at 110–120°, and then carefully ignite to expel ammonium salts. Weigh the residue of alkali chlorides. Add 25 ml of dry acetone and 1 drop of concentrated hydrochloric acid. Stir well, allow the residue to settle, and decant through a filter. Wash the residue 3 times with 5-ml portions of acetone. Dissolve the residue in a little water and again evaporate and extract with acetone. If necessary repeat this once more. Evaporate the combined filtrates in a weighed platinum or quartz dish to remove the acetone, take up the residue in a little water, add some sulfuric acid, evaporate dry, and weigh as $LiSO_4$.

Indirect Determination of Lithium and Sodium or Lithium and Potassium

The mixture of the two chlorides is weighed and the chlorine determined either gravimetrically or volumetrically.

Separation of Potassium, Rubidium, and Cesium

Rubidium and cesium, when either is present alone, can be determined by any of the methods described for potassium. The solubility of the chloroplatinates, cobaltinitrites, and perchlorates of rubidium and cesium is less than that of the potassium salt. The qualitative separation described in Vol. I of this book is probably as good as any that has been devised. In this procedure, lead is first removed by precipitation with lead nitrate in the presence of dilute nitric acid. After filtering off the lead sulfate, the excess lead is removed by saturating the solution with hydrogen sulfide. The cesium, rubidium, and potassium are then precipitated together as perchlorates, as described on pp. 273, 274 for the determination of potassium, and the filtrate from this precipitation will contain sodium and lithium. The perchlorates of cesium, rubidium, and potassium are dissolved in a little hot water, converted into cobaltinitrites, as described on p. 270, and filtered off. This precipitate, together with a little sodium nitrite solution, is heated until the mass fuses and effervesces no more, the residue is taken up in water and a little dilute acetic acid, and the black cobalt oxide residue is rejected. The solution of alkali nitrites is treated with sodium nitrite and bismuth nitrate solution to precipitate $Cs_2NaBi(NO_2)_6$ and Rb_2NaBi $(NO_2)_6$, leaving potassium nitrite in solution. The precipitate is treated with hydrochloric acid and, in the resulting solution, cesium is precipitated as $Cs_2Sb_2Cl_9$. After filtering off this precipitate, the rubidium is precipitated as $RbHCl_2I_2O$, and finally converted into $Rb_2NaBi(NO_2)_6$ again. The separation is imperfect because the difference in the solubility of the corresponding cesium and rubidium salts is

not great enough to permit a complete separation. The procedure can be carried out and approximately correct results obtained quantitatively if more time is allowed for the complete precipitation of the cobaltinitrites and of the alkali-bismuth nitrites.

The following procedure, which is based upon one proposed by Strecker and Diaz,[1] gives fairly satisfactory results when but little potassium is present.

Procedure. Dissolve the chlorides,[2] free from ammonium salt, in a little water, and slowly add, while stirring, a mixture of concentrated hydrochloric acid diluted with twice as much 95 per cent alcohol. Filter off the precipitated KCl (and NaCl if present), wash with absolute alcohol, dry at 110°, and weigh. Heat the filtrate to boiling and treat with a boiling-hot, concentrated solution of $SnCl_4$ which has been dissolved in a mixture of 1 part concentrated hydrochloric acid and 2 parts alcohol. Allow to cool, and after 4 hours filter off the precipitate of Cs_2SnCl_6 and Rb_2SnCl_6, wash with absolute alcohol, dry at 100°, and weigh. If it is desired to determine the potassium, treat the filtrate with perchloric acid, and determine the potassium not removed as chloride by the treatment with hydrochloric acid and alcohol. Add the corresponding weights of both precipitates to obtain the total potassium content. Dissolve the weighed chlorostannates in 5 per cent tartaric acid solution, saturate with hydrogen sulfide, and filter off the stannic sulfide precipitate. Evaporate the filtrate to dryness, and ignite carefully to destroy the tartaric acid.

Treat the residue with an equal weight of $FeCl_3$, and dissolve in as little water as possible. Add 5 ml of glacial acetic acid for each 0.1 g of mixed chlorides and heat just to boiling. Add a cold 30–40 per cent solution of $ShCl_3$ in glacial acetic acid, digest 1 hour on the water bath, cool, and allow to stand for at least 12 hours. Filter through a Gooch, Munroe, or glass filtering crucible, and wash the precipitate of $Cs_3Sb_2Cl_9$ with a 5–10 per cent solution of $ShCl_3$ in glacial acetic acid.

If considerable rubidium was present, it is necessary to dissolve this precipitate in hydrochloric acid and repeat the precipitation with $ShCl_3$. The second precipitate should be pure.

Dissolve the final precipitate of $Cs_3Sb_2Cl_9$ in hydrochloric acid, dilute until it is approximately 0.3 N in acid, disregarding any $ShOCl$ precipitate that may form, saturate with hydrogen sulfide, filter off the Sb_2S_3, evaporate the filtrate to dryness, and determine the cesium as $CsClO_4$ as described for the determination of potassium on p. 274. Deduct the corresponding weight of Cs_2SnCl_6 from the weighed mixture obtained above to obtain the weight of Rb_2SnCl_6.

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[1] *Z. anal. Chem.*, **67**, 321 (1925).

[2] Perchlorates can be converted into chlorides by careful ignition.

AMMONIUM, NH$_4$.   Mol. Wt. 18.04

Forms: NH$_3$, NH$_4$Cl, (NH$_4$)$_2$PtCl$_6$, Pt, N$_2$

Two cases are to be distinguished: (1) the ammonium is present as chloride in aqueous solution; (2) the ammonium is present in solution together with other cations and anions.

1. The Solution Contains Only NH$_4^+$ and Cl$^-$ Ions

In this case the solution can be evaporated to dryness and the residue of ammonium chloride weighed; or the ammonium can be precipitated as (NH$_4$)$_2$PtCl$_6$ and the precipitate weighed; or the ammonium chloroplatinate can be ignited and the residue of platinum weighed.

(a) Determination as NH$_4$Cl

Add concentrated HCl to the aqueous solution and evaporate to a small volume on the water bath at as low a temperature as possible, transfer the solution to a crucible, evaporate on the water bath to dryness, and heat the covered crucible to constant weight in a drying oven at 105°. Good results are obtained, but they are always a little low. On evaporating the aqueous solution some NH$_4$Cl is driven off, and the amount lost increases in proportion to the quantity of water used and the temperature at which the evaporation takes place. In cold, aqueous solution, ammonium chloride is largely ionized, NH$_4$Cl $\rightarrow$ NH$_4^+$ + Cl$^-$. As the temperature is raised, hydrolysis takes place to an appreciable extent, NH$_4$Cl + H$_2$O $\rightarrow$ NH$_4$OH + HCl, and NH$_3$ evaporates from the ammonium hydroxide noticeably faster than does hydrogen chloride. If, however, a little hydrochloric acid is added to the solution the hydrolysis is prevented and the loss of NH$_3$ is reduced to a minimum. The ammonium chloride must be dried in a covered crucible at 105°, as otherwise a small quantity of the salt will be lost, but this loss is small in comparison with the possible loss during the evaporation.

(b) Determination as (NH$_4$)$_2$PtCl$_6$

On heating (NH$_4$)$_2$PtCl$_6$ to 130° the salt is unchanged. An aqueous solution containing HCl, NH$_4$Cl, and an excess of H$_2$PtCl$_6$ can be evaporated to dryness without appreciable loss of NH$_3$. To the aqueous solution of ammonium chloride, therefore, add an excess of chloroplatinic acid and a little hydrochloric acid. Evaporate to dryness at as low a temperature as possible. Pour absolute alcohol over the residue to dissolve the excess of H$_2$PtCl$_6$, break up the crystals with a stirring rod, and filter through a Gooch crucible. Dry at 130° and weigh.

(c) Determination as Platinum

Instead of weighing the $(NH_4)_2PtCl_6$ as such, it can be decomposed by ignition and the weight of the residual platinum determined. As ammonium chloroplatinate decrepitates strongly on being heated, the ignition must take place in a large porcelain crucible, which is provided with a close-fitting cover. The precipitate must be heated gradually at first to prevent loss. It is best ignited according to the directions of Rose. Place the precipitate and filter in the crucible with the filter paper on top, cover the crucible, and heat over a small flame until the paper is completely charred without allowing the vapor to escape visibly from the crucible. Then heat the crucible with a hotter flame, allowing free access of air into the inclined crucible, until the charred filter is completely consumed.

2. The Ammonium Is Present Together with Other Cations and Anions in Solution or in Solid Form

The aqueous solution is made alkaline by the addition of sodium hydroxide, and the liberated ammonia is distilled off through a condenser and absorbed in acid. The solution thus obtained can be analyzed by one of the above methods, but the usual procedure is to finish the analysis by titration. For the absorption of the ammonia a measured volume of standard hydrochloric or sulfuric acid can be used, in which case the determination is based upon the titration of the excess acid with standard sodium hydroxide to a methyl red end point. It is also convenient to absorb the ammonia in boric acid solution; this acid serves to prevent the escape of ammonia by forming ammonium borate, but the boric acid is such a weak acid that it does not affect the methyl red and ammonium borate titrates with $0.5 N$ HCl to a methyl red end point as if it were a solution of free ammonia.

The method was described in Vol. I for the detection of ammonia in water. For very small quantities of ammonia, special pains must be taken to use water containing no ammonia or ammonium salt and to finish the analysis by comparing the color produced by nesslerization of an aliquot part of the entire distillate with that obtained with a series of solutions containing known quantities of ammonia. For the determination of ammonium in a solid the ammonia is usually distilled off after adding alkali hydroxide and absorbed in a measured volume of standard acid or in boric acid (see Chapter XIV).

Separation of Magnesium from the Alkalies

The methods of Schmitz and of Epperson serve to separate magnesium from the alkalies if the determination of magnesium alone is desired. If it is desired to determine magnesium and the alkalies in one and the same sample, it is best to proceed as follows:[1]

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[1] Gooch and Eddy, *Z. anorg. Chem*, **58**, 427 (1908).

Schaffgottsch Method for Precipitating Magnesium[1]

The method is based upon the fact that magnesium can be precipitated quantitatively, by means of an alcoholic solution of ammonium carbonate, as crystalline magnesium ammonium carbonate, $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 6H_2O$.

Preparation of the Precipitant. Saturate a mixture of 180 ml concentrated ammonia, 800 ml water, and 900 ml absolute alcohol with commercial ammonium carbonate. Shake the mixture occasionally, and after several hours filter off the excess of carbonate.

Procedure. Treat the neutral solution containing only magnesium and the alkalies (lithium must not be present), preferably in the form of chlorides, with an equal volume of absolute alcohol and then with an excess of the ammonium carbonate reagent. Stir vigorously for a few minutes and allow to stand for at least half an hour. Filter through a Gooch or Munroe crucible. Wash with the precipitant, dry, ignite, and weigh as MgO.

If considerable alkali is present the precipitate always contains a small quantity of it. In such cases dissolve the precipitate in hydrochloric acid, evaporate the solution to dryness, take up the residue in a little water, and repeat the precipitation.

Evaporate the combined filtrates to dryness and determine the alkalies as described on pp. 280–286.

Barium Hydroxide Method

If it is desired to separate magnesium from the alkalies in order that the alkalies may be determined, the magnesium can be precipitated as magnesium hydroxide, from a solution free from ammonium salts, by the addition of barium hydroxide solution. The barium is then removed by ammonium carbonate and the alkalies determined in the filtrate. For the detailed description of this method see Chapter XII, "Silicate Analysis." *Even in this case, however, the use of the Schaffgottsch method of separating magnesium from the alkalies is more satisfactory.*

Magnesium can also be separated from the alkalies by means of 8-hydroxyquinoline, mercuric oxide, amyl alcohol, or a mixture of alcohol and ether.

Mercuric Oxide Method

When magnesium chloride is heated with mercuric oxide, magnesium oxide and mercuric chloride are formed. The mercuric chloride and the excess mercuric oxide are easily removed. The oxides of mercury and of magnesium are insoluble, but the alkali oxides are soluble in water.

Prepare a suspension of mercuric oxide in water as follows: Resublime pure mercuric chloride from a mixture containing one-tenth of its weight of mercuric oxide. Dissolve the sublimate in sufficient water to make a saturated solution (about 40 ml

[1] *Pogg. Ann.*, **104**, 482 (1858)

water per gram of $HgCl_2$). Heat the solution to boiling, and slowly pour it into an excess of hot 10 per cent sodium hydroxide solution. Let the mercuric oxide precipitate settle, wash by decantation with hot water, and finally on a filter until the wash water is free from chloride. Mix with water and keep in a ceresin or paraffin-lined bottle.

Procedure. Evaporate the solution containing magnesium and alkalies to dryness in a platinum, porcelain, or quartz dish, and remove ammonium salts by heating the residue carefully. Avoid heating strongly as this may cause volatilization of sodium chloride. Treat the residue with a little water and mix it with some yellow mercuric oxide suspension. Add this slowly, while stirring, until the mercuric oxide no longer dissolves. Evaporate to dryness, add a few drops of water, and again heat. Repeat this once or twice more. Finally heat under a good hood until the poisonous fumes of mercuric chloride cease coming off. It is inadvisable to heat until all mercuric oxide is removed as this may result in loss of alkali. Treat the residue with hot water, filter, and wash. If more than 1 per cent of magnesium is present, dissolve the residue in a little hot hydrochloric acid and repeat the above treatment. Finally transfer the residue of MgO and Hg to a weighed crucible and heat under a good hood until all HgO has been removed.

Amyl Alcohol and Ether-Alcohol Methods

These methods differ from the preceding ones inasmuch as the alkalies are precipitated instead of the magnesium. In the absence of lithium, the amyl alcohol method developed by R. B. Riggs[1] can be used. It is similar to the method of Gooch for separating lithium from the other alkalies which has already been discussed. The use of a mixture of alcohol and ether has been recommended by S. Palkin.[2] Lithium, if present, will accompany the magnesium in both cases.

[1] *Am. J. Sci.*, [3] **44**, 103 (1892).
[2] *J. Am. Chem. Soc.*, **38**, 2326 (1916); **42**, 1618 (1920).

CHAPTER VI

GROUP I OF ANIONS

HYDROCHLORIC, HYDROBROMIC, HYDRIODIC, HYDROCYANIC,
FERROCYANIC, FERRICYANIC, THIOCYANIC,
AND HYPOCHLOROUS ACIDS

HYDROCHLORIC ACID, HCl. Mol. Wt. 36.46

Form: Silver Chloride, AgCl

1. The chlorine is present in solution either as free hydrochloric acid or as a chloride soluble in water.

2. It is present in the form of an insoluble chloride.

1. The Chloride Is Present in Aqueous Solution

If only metals of the alkali or alkaline-earth groups are present, make the cold solution slightly acid with nitric acid, and slowly add silver nitrate with constant stirring until the precipitate coagulates and further addition of the reagent produces no more precipitation. Now heat the liquid to boiling, allow the precipitate to settle in the dark, filter through a Gooch crucible, and treat the AgCl precipitate exactly as described in the determination of silver, p. 50.

If the aqueous solution contains a chloride of a heavy metal, it is not always possible to follow the above procedure. If, for example, substances are present which on boiling are changed to insoluble basic salts, it is evident that the precipitate of silver chloride would be contaminated with these substances and too high results would be obtained. This is particularly true of stannic and ferric salts. Ferrous salts, on the other hand, if only a little nitric acid is present, reduce silver nitrate to metallic silver on heating the solution; if enough nitric acid is present to prevent the reduction to silver, the danger of forming basic salts still remains. In such cases the precipitation is effected as before from a cold solution and the subsequent heating is omitted.

Invariably, however, it is better first to remove the heavy metal by precipitation with ammonia, caustic soda, or sodium carbonate.

2. Analysis of an Insoluble Chloride

Boil the substance with sodium carbonate solution[1] (free from chloride), filter, and determine the chlorine in the filtrate as described above.

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[1] Mercuric chloride is decomposed only slowly by sodium carbonate solution but is readily acted upon by potassium or sodium hydroxide.

Some chlorides, e.g., silver chloride, many minerals such as apatite,[1] sodalite, and rocks containing them are not decomposed by boiling with sodium carbonate. Such substances must be *fused* with sodium carbonate.

Mix silver chloride with 3 times as much sodium carbonate and heat in a porcelain crucible until the mass has sintered together. Extract with water, filter off the insoluble silver, and determine the chlorine in the filtrate as under 1.

For the determination of chlorine in rocks, fuse 1 g of the finely powdered material with 4 or 5 times as much sodium carbonate (or with a mixture of equal parts sodium and potassium carbonates) at first over a Bunsen burner, afterward over a Méker burner or the blast lamp. Extract the melt with hot water. After cooling, add methyl orange indicator solution, acidify with nitric acid, and allow to stand over night. If silicic acid has precipitated out by the next morning, add a little ammonia, boil the solution, filter, and wash with hot water. Add a little nitric acid to the cold filtrate and determine the chlorine as above.

If there is no separation of silicic acid on acidifying the water extraction of the fusion with nitric acid,[2] precipitate the chlorine at once from the cold solution.

Free Chlorine

If it is desired to determine gravimetrically the amount of chlorine in a sample of chlorine water, it is not feasible simply to add silver nitrate, for not all the chlorine is precipitated as silver chloride; a part of it remains in solution as soluble chloric acid:

$$3Cl_2 + 3H_2O + 5AgNO_3 = 5AgCl + HClO_3 + 5HNO_3$$
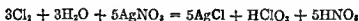
The chlorine, therefore, must be changed to hydrochloric acid or to one of its salts before attempting to precipitate with silver nitrate. This may be accomplished in several ways:

1. Transfer a definite amount of the chlorine water by means of a pipet to a flask containing ammonia water, and after mixing heat the solution to boiling. After cooling, acidify with nitric acid and precipitate with silver nitrate. The ammonia converts the chlorine to ammonium chloride:

$$8NH_4OH + 3Cl_2 = 6NH_4Cl + N_2 + 8H_2O$$

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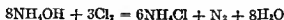
[1] According to Jannasch, chlorine in apatite may be determined by treating the finely powdered mineral with nitric acid and silver nitrate on the water bath Everything goes into solution with the exception of silver chloride, which is filtered off and weighed. (This does not apply to a sample of apatite contaminated with silica or silicates.)

[2] According to W. F. Hillebrand, no separation of silicic acid is to be feared from 1 g of the substance.

2. Treat the chlorine water with an excess of sulfurous acid, make the solution ammoniacal, add hydrogen peroxide, and boil the liquid until the excess of hydrogen peroxide is removed. Cool, acidify with nitric acid, dilute with water, and precipitate the chlorine by means of silver nitrate.

3. Treat the chlorine water with dilute sodium hydroxide solution, and add an aqueous solution of sodium arsenite (arsenic trioxide dissolved in sodium carbonate) until a drop of the liquid will not turn a piece of iodo-starch paper blue. Then make acid with nitric acid and precipitate the chlorine by a soluble silver salt.

If the solution contains both free chlorine and hydrochloric acid determine the total chlorine by one of the above methods, and the free chlorine in a separate sample by a volumetric process (see Chapter XV, "Iodimetry").

Determination of Chlorine in Non-Electrolytes (Organic Compounds)

(a) Method of Carius[1]

Principle. The method is based upon the fact that all organic compounds are decomposed by heating with concentrated nitric acid at a high temperature under pressure. If the substance contains halogen, sulfur, phosphorus, or arsenic, it is first set free as such, but on account of the reducing action of the nitrous acid formed it is then changed over into its hydrogen compound. This, however, is partly oxidized by the nitric acid. The reaction is therefore a reversible one. If, on the other hand, the substance is heated under the same conditions with nitric acid in the presence of silver nitrate, the halogen hydride is converted into silver halide as fast as it is formed and the halogen is quantitatively changed into its silver salt. Sulfur, phosphorus, and arsenic are oxidized in the same way to sulfuric, phosphoric, and arsenic acids, and any metals present form nitrates.

Procedure. Take a tube made of difficultly fusible glass about 50 cm long, 2 cm in diameter, with walls about 2 mm thick. Seal one end, clean thoroughly, and dry by drawing air through it.

Transfer about 0.5 g of powdered silver nitrate (of substances rich in halogen as much as 1 g may be used) to the tube by pouring the powder through a cylinder made by rolling up a piece of glazed paper and shoving the paper into the tube until it reaches about the middle of it. Pour into the tube, through a funnel whose stem is about 40 cm long, 2–5 ml of pure nitric acid (d 1.5) free from chlorine. In this way only the lower half of the tube is wet with the acid. Incline the tube to one side and introduce a small glass tube, closed at one end and containing from 0.15 to 0.2 g of the substance (this smaller tube should be about 5 cm long and 5 mm wide). As soon as the tube containing the substance has reached the acid, it remains suspended (Fig. 41, a).

Fig. 41.

[1] Ann. Chem. Pharm., 136, 129 (1865), and Z. anal. Chem., 4, 451 (1865).

It is very important that the substance should not come in contact with the acid before the tube is closed at the upper end, as otherwise there is likelihood of losing some halogen.

Now heat the upper end of the tube very cautiously in the flame of the blast lamp until the tube begins to soften and thicken (Fig. 41, b). Then draw out into a thick-walled capillary 3–5 cm long, and fuse the end together (Fig. 41, c).

After the tube has become cold, envelop it in asbestos paper, carefully shove it into the iron mantle of a " bomb furnace," and gradually heat. Aliphatic substances are usually decomposed by heating 4 hours at 150–200°; substances of the aromatic series usually require from 8 to 10 hours' heating at 250–300°, and for some substances an even longer heating at a higher temperature is necessary. The time and temperature must be found out for each substance by experiment. The decomposition is complete when on cooling the contents of the tube neither crystals nor drops of oil are to be recognized.[1] Regulate the heating so that after 3 hours the temperature of about 200° is reached, after 3 hours more 250–270°, and finally after another 3 hours a temperature of about 300°.[2] After the heating is finished, allow the tube to cool completely in the furnace, remove the iron mantle together with the tube, and by slightly inclining the mantle bring the capillary of the tube out into the open air. Usually a drop of liquid will be found in the point of the capillary. In order not to lose this, carefully heat the outer point with a free flame, and by this means drive back the liquid into the other part of the tube. Now heat the point of the capillary more strongly[3] until the glass softens, and a hole is blown in the soft glass as a result of the pressure within the tube. The gas escapes with a hissing sound. When the contents of the tube are at the atmospheric pressure, make a scratch upon it with a file just below the capillary, and touch this with a hot glass rod, whereby the tube usually breaks and the upper part can be removed. Now carefully pour out the contents of the tube into a fairly large beaker, without breaking the little tube into which the substance was weighed, and wash out the inner part of the tube as well as

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[1] Sometimes, with substances rich in sulfur, crystals of nitrosyl sulfuric acid are formed which adhere to the sides of the tube. They are easily distinguished from crystals of the undecomposed substance.

[2] Such a high pressure is often attained that the tube bursts as soon as it is heated very hot. In such cases heat to only 200°, allow to cool, open the capillary, and release the pressure. Then fuse together again and heat to the desired temperature.

[3] Before heating, the tube and the hand should be wrapped in a towel to avoid accidents.

its capillary with water. Dilute the liquid in the beaker to about 300 ml and heat to boiling. After cooling, filter off the insoluble silver halide through a Gooch crucible and weigh after washing and drying at 130°.

If it is thought that the precipitate is contaminated by fragments of broken glass, as often happens even with careful work, decant the clear liquid through a filter, wash the residue by decantation with very dilute nitric acid to the disappearance of the silver reaction, and dissolve the residue (except when it is silver iodide) in warm ammonia water. Filter the solution through the same filter, but collect the filtrate this time in a fresh beaker. After washing the filter with dilute ammonia, acidify the filtrate with nitric acid, heat to boiling, and, after allowing the silver chloride or bromide to settle in the dark, filter through a Gooch crucible, dry at 130°, and weigh.

Silver iodide cannot be dissolved in ammonia and in this way separated from splinters of glass. Therefore, filter off the precipitate, together with the glass, through an ordinary washed filter (not a Gooch crucible), wash with dilute nitric acid, then once with alcohol in order to remove the nitric acid, and dry at 100°. Transfer as much of the precipitate as possible to a watch glass, burn the filter, and drop the ash into a weighed porcelain crucible. Add a little dilute nitric acid (to change any reduced silver into the nitrate), evaporate off the liquid on the water bath, add a few drops of water and a drop of pure hydriodic acid, and again evaporate the contents of the crucible to dryness. Now add the main part of the precipitate, heat until it begins to fuse, and weigh. Cover the mass in the crucible with pure dilute sulfuric acid, add a piece of chemically pure zinc, and allow the crucible to stand over night. After this time the silver iodide will be completely reduced to metallic silver. Remove the zinc, and wash the residue by decanting several times with water until the iodide reaction can no longer be detected. Warm the residue with dilute nitric acid upon the water bath, in order to dissolve the silver; filter the solution through a small filter. Wash the filter with water and dry; ignite it in a crucible and weigh the residue (the glass). This second weight deducted from the former gives the amount of silver iodide present.

This method is also suitable for obtaining lead and mercury from organic compounds in a form which can be precipitated by hydrogen sulfide.

The method of Carius is by far the best for the determination of halogens in organic substances when only one of the halogens is present. If two or three of them are present at the same time, the "lime method" is to be preferred.

(b) *The Lime Method*

Into a glass tube made of difficultly fusible glass (about 40 cm long, 1 cm wide, and closed at one end), introduce a layer of lime (free from chloride) from 5 to 6 cm long, then about 0.5 g of substance, and finally 5 cm more of lime. Mix the substance thoroughly with the lime by means of a copper wire wound into a spiral. Nearly fill the tube with lime, place on its side, and gently tap, so that a small canal is formed above the lime. Place the tube in a small combustion furnace (cf. p. 355) and heat. First heat the front end of the tube, free from substance, to a dull redness, then the back end, and afterwards light the other burners, one after another, until finally the whole tube is at a dull red heat. After cooling, transfer the contents of the tube to a large beaker and dissolve the lime in dilute nitric acid free from chlorine. Filter off the carbon, and precipitate the halogen with silver nitrate.

If the lime contains calcium sulfate, this is reduced to sulfide, so that some silver sulfide is likely to be precipitated with the silver halide. In this case treat the solution with hydrogen peroxide (free from halogen) before enough nitric acid has been added to make the solution acid, boil the liquid to remove the excess of the reagent, then acidify, filter, and precipitate with silver nitrate.[1] In the analysis of substances rich in nitrogen, it is possible that some soluble calcium cyanide will be formed. In this case care must be taken that the silver precipitate contains no silver cyanide (cf. "Separation of Hydrocyanic Acid from Halogen Hydride," p. 303).

(c) *The Sodium Peroxide Method*

Heat 0.2–0.3 g of the substance with a mixture of 10 g of powdered potassium hydroxide and 5 g of sodium peroxide in a nickel or iron crucible. Heat first in the hot closet at 85°. After some time remove the crucible from the closet and heat over a small flame, gradually raising the temperature until the flux is melted. Cool, extract the melt with water, filter, and determine the halogen as silver salt after adding nitric acid.

The fusion in the NaOH and Na_2O_2 can be carried out conveniently in a Parr bomb.

Remark. For an excellent volumetric method for determining chlorine see the Volhard method in Chapter XVII.

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[1] W. Biltz (*Chem. Ztg.*, 1903, Rep. 142) separates the halides from sulfide by treating the precipitated silver salts with an ammoniacal sodium thiosulfate solution, whereby the silver halide goes into solution, from which the silver is precipitated as silver sulfide, by adding ammonium sulfide, and determined as silver.

HYDROBROMIC ACID, HBr. Mol. Wt. 80.92

Form: Silver Bromide, AgBr

Hydrobromic acid is determined exactly the same as hydrochloric acid. This is also true of the determination of free bromine and of bromine in non-electrolytes.

HYDRIODIC ACID, HI. Mol. Wt. 127.93

Forms: Silver Iodide, AgI, and Palladous Iodide, PdI₂

(a) Determination as Silver Iodide

The determination of hydriodic acid is carried out in exactly the same way as the analysis of hydrochloric acid. If it is desired to filter the silver iodide through an ordinary washed filter instead of through a Gooch crucible, the procedure described on p. 51 or 295 is used, converting the reduced metal to iodide by dissolving in nitric acid and adding hydriodic acid. If no hydriodic acid is available, place the main portion of the precipitate in a weighed porcelain crucible and heat until it begins to melt, and then weigh. Place the filter ash in another crucible, and treat with nitric and hydrochloric acids, whereby the silver and any unreduced iodide are changed to silver chloride. Weigh the silver chloride and add the equivalent amount of silver iodide to the weight of the main part of the precipitate.

(b) Determination as Palladous Iodide

This important method for the separation of iodide from bromide and chloride is carried out as follows:

Make the solution acid with hydrochloric acid, and add palladous chloride solution until no more precipitate is formed. After allowing to stand one or two days in a warm place, filter off the brownish black precipitate of palladous iodide through a Gooch crucible, or through a tared filter that has been dried at 100°, wash with warm water, dry at 100°, and weigh as PdI₂.

According to Rose, the PdI₂ may be changed to palladium by igniting in a current of hydrogen, and from the weight of the palladium the amount of iodine calculated.

SEPARATION OF THE HALIDES FROM ONE ANOTHER

1. Separation of Iodide from Chloride

(a) The Palladous Iodide Method

Determine the iodide as palladous iodide, and in a second sample determine the sum of the chloride and iodide from the weight of their insoluble silver salts.

(b) Method of Gooch

This method depends upon the fact that, in a dilute acid solution of the three halides, nitrous acid reacts only with the iodide:

$$2KI + 2KNO_2 + 4H_2SO_4 = 4KHSO_4 + 2NO + 2H_2O + I_2$$
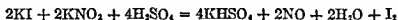
Iodine is liberated and escapes from the solution on boiling. In one sample, therefore, precipitate the halogens together in the form of their silver salts; in a second sample determine the amount of the chlorine after setting free the iodine by means of nitrous acid, and determine the amount of iodine by difference. In order to obtain correct results by this method, the solution must be very dilute when it is boiled to expel the iodine; otherwise some chlorine escapes.

Procedure. Dissolve 0.5 g of the halide mixture in 600 ml of water in a liter flask, treat with 2–3 ml of dilute sulfuric acid, add 0.5–1 g of solid potassium nitrite (free from halide), and boil the solution until entirely colorless; usually this is accomplished in about three-quarters of an hour. Then add silver nitrate solution, and allow the resulting precipitate to settle. Filter through a Gooch crucible, and weigh.

2. Determination of Bromide together with Chloride

Principle. In this indirect method the sum of the weights of the silver salts of the two halogens is first determined and afterwards the silver bromide is converted to silver chloride by heating in a current of chlorine.

Procedure. To the neutral solution containing about 0.5 g of halides add a little nitric acid (free from chlorine) and precipitate in the cold by the addition of a slight excess of silver nitrate. Heat the liquid to boiling, with frequent stirring, cool after the precipitate has coagulated, and filter off the precipitate into a 15-cm-long asbestos filter tube made of difficultly fusible glass. Dry the precipitate at 150°, and weigh after cooling.

For the transformation of the bromide into chloride, shove the asbestos forward a little in the tube by means of a glass rod (in order that the gas may pass through it more readily), fasten the tube in a slightly inclined position, and pass a current of dry chlorine gas through it. At

the same time cautiously heat the tube by moving a small flame back and forth. During the first half hour the precipitate should not be heated hot enough to melt it; finally, however, raise the temperature until it *begins* to melt, after which replace the chlorine by air, cool, and again weigh.

If p represents the weight of silver chloride and bromide first obtained, q the weight after the precipitate has been completely changed to chloride, x the weight of silver chloride in the first precipitate, and y the weight of silver bromide, then $x + y = p$ and $x + \dfrac{AgCl}{AgBr} y = q$.

Since $\dfrac{AgCl}{AgBr} = 0.7633$, the solution of the above two equations gives $y = 4.225(p - q)$ and $x = p - y$, from which the percentage of chlorine and bromine can be computed.

3. Determination of Iodide together with Chloride

The same procedure is used as above described.

If p represents the weight of silver iodide + silver chloride, q the weight after the silver has been converted to chloride, x the weight of silver chloride, and y the weight of silver bromide in the first precipitate, $y = 2.567(p - q)$ and $x = p - y$.

4. Determination of Bromide in the Presence of Iodide

In this case p represents the weight of the silver bromide and silver iodide, q as before the corresponding weight of silver chloride, x the weight of silver iodide in the first precipitate, and y the weight of silver bromide,

$$x + y = p, \qquad \frac{AgCl}{AgI} x + \frac{AgCl}{AgBr} y = q$$
$$x = 4.994p - 6.545q$$
$$y = p - x$$

5. Determination of Iodide, Bromide, and Chloride

In one portion of the substance determine the weight p of silver salts obtained by precipitation and change this over to silver chloride of weight q. In another portion of the same weight of original substance, determine the weight t of palladous iodide corresponding to the iodine content. Then, if x represents the weight of silver chloride and y the weight of silver bromide in the first precipitate, the following relationships hold:

$1.303t$ = weight of silver iodide in the first silver precipitate and $0.7951t$ is the corresponding weight of silver chloride.

$p - 1.303t$ = weight of silver bromide and silver chloride in the first precipitate.

$q - 0.7951t$ = weight of silver chloride in the second precipitate equivalent to the chloride and bromide.

$$x + y = p - 1.303t; \quad x + 0.7633y = q - 0.7951t$$
$$y = 4.224\,[(p - 1.303t) - (q - 0.7951t)]$$
$$x = p - 1.303t - y$$

Instead of determining the iodine as palladous iodide it may be removed as on p. 298, b, by treatment with nitrous acid and the weight of the silver bromide + silver chloride obtained.

Another method[1] depends upon the fact that treatment of silver halides with potassium dichromate and concentrated sulfuric acid causes the following decompositions:

$$6AgCl + K_2Cr_2O_7 + 14H_2SO_4 = 6AgHSO_4 + 2KHSO_4 + 2Cr(HSO_4)_3 + 7H_2O + 3Cl_2 \uparrow$$
$$6AgBr + K_2Cr_2O_7 + 14H_2SO_4 = 6AgHSO_4 + 2KHSO_4 + 2Cr(HSO_4)_3 + 7H_2O + 3Br_2 \uparrow$$
$$2AgI + 2K_2Cr_2O_7 + 18H_2SO_4 = 2AgHSO_4 + 4KHSO_4 + 4Cr(HSO_4)_3 + 8H_2O + 2HIO_3$$
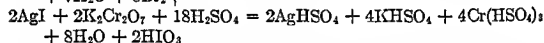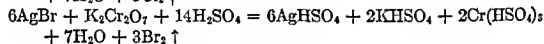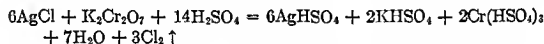
All the bromine and chlorine can be distilled off, but the silver and all the iodine remain behind. By the introduction of SO_2 into the diluted acid, the iodic acid is reduced to hydriodic acid and silver iodide precipitates. After this has been filtered off, the remaining silver can be precipitated as iodide. Thus for the determination of the three unknowns, three simultaneous equations can be formulated.

Procedure. Precipitate a mixture of silver chloride, bromide, and iodide in the usual manner, filter into a small asbestos filtering tube, and weigh after drying at 150°. Call the weight of original substance A and that of the mixed halides a. Place the dry precipitate together with the asbestos in an Erlenmeyer flask, and for each 0.3 g of silver salt add 2 g of pure potassium dichromate and 30 ml of concentrated sulfuric acid. Heat 2 hours at 95°. Toward the last, pass a stream of air through the liquid until all the chlorine and bromine have been expelled. The decomposition takes place more rapidly if the precipitate is treated with the oxidizing mixture without drying it except by suction, but this necessitates the determination of the mixed silver salts in a separate sample. After the oxidation of the silver salts is complete,

[1] Bech, Chem.-Ztg., 39, 405 (1915), Baubigny, Compt. rend., 127, 1219 (1898).

dilute with 300 ml of water, filter off the asbestos, and to the filtrate add sodium bisulfite solution drop by drop until a faint permanent odor of sulfur dioxide is obtained. Filter off and weigh the silver iodide precipitate; call this weight b. In the filtrate precipitate the rest of the silver by adding potassium iodide. Call this weight c. Compute the percentages of chlorine, bromine, and iodine as follows:

$$\frac{54.06b}{A} = \text{per cent iodine}$$

$$\frac{63.8c - 79.7(a - b)}{A} = \text{per cent chlorine}$$

$$\frac{179.8(a - b) - 109.7c}{A} = \text{per cent bromine}$$

HYDROCYANIC ACID, HCN. Mol. Wt. 27.03

Forms: Silver Cyanide, AgCN, and Metallic Silver, Ag

Free hydrocyanic acid as well as the cyanides of the alkalies and alkaline earths are decomposed quantitatively by silver nitrate with the formation of insoluble silver cyanide.

If, therefore, it is desired to determine gravimetrically the amount of cyanide present in an aqueous solution of hydrocyanic acid or of an alkali cyanide, treat the cold solution with an excess of silver nitrate, stir, make faintly acid with nitric acid, allow the precipitate to settle, filter through a weighed filter, dry at 110°, and weigh. To confirm the result, place the silver cyanide in a porcelain crucible, burn the filter in a platinum spiral, add its ash to the main portion of the precipitate, and ignite the contents of the crucible, at first gently and finally more strongly but not enough to melt the silver. Cool and weigh the silver.

By the decomposition of the silver cyanide, difficultly volatile paracyanide is formed, but this is gradually burned away by igniting the contents of the open crucible.

Example: Determination of Hydrocyanic Acid in Bitter-Almond Water. Bitteralmond water contains cyanogen as free hydrocyanic acid and as ammonium cyanide, but the greater part is present as mandelic acid nitrile, $C_6H_5CH(OH)CN$, which is not decomposed in aqueous solution by means of silver nitrate, but is readily acted upon by it if the solution is made ammoniacal after the addition of the silver nitrate and then made acid.

The gravimetric determination of the cyanogen present is performed according to the method of Feldhaus[1] as follows:

[1] Z. anal. Chem., 3, 34 (1864).

Treat 100 g of bitter-almond water with 10 ml of a 10 per cent silver nitrate solution, add 2–3 ml of concentrated ammonium hydroxide and immediately acidify with nitric acid. Allow the precipitate to settle, and determine the HCN as described above.

Liebig's volumetric method is much more satisfactory for this determination (see Chapter XVII).

If it is desired to determine the amount of cyanogen in a solid alkali cyanide, dissolve a weighed amount of the salt in water containing silver nitrate, and make the solution acid with nitric acid and treat the precipitate as above.

If the cyanide is dissolved in water before the addition of the silver nitrate, there is always a slight loss of hydrocyanic acid.

Some complex cyanides are quantitatively decomposed by silver nitrate, e.g., those of nickel, zinc, and copper (the last only slowly); others such as the ferro- and ferricyanides of the alkalies (and mercuric cyanide) are not.

Determination of Cyanogen in Mercuric Cyanide, Method of Rose

Mercuric cyanide is a non-electrolyte and is consequently not precipitated by silver nitrate, but it is acted upon by hydrogen sulfide with the formation of insoluble mercuric sulfide and hydrocyanic acid:

$$Hg(CN)_2 + H_2S = HgS + 2HCN$$
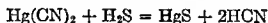
This reaction, however, cannot take place in neutral or acid solutions on account of the volatility of the hydrocyanic acid; it must be performed in an alkaline solution. In order to avoid the introduction of an excess of hydrogen sulfide into the solution, the following procedure is necessary:

Treat the aqueous solution of the mercuric cyanide with about twice as much zinc sulfate dissolved in ammonia. If this should cause a turbidity, add enough ammonia to clear it up and slowly add hydrogen sulfide water. This causes at first a brown precipitate which becomes black on stirring. Continue the addition of hydrogen sulfide water until the upper liquid shows a *pure white* precipitate of zinc sulfide. The zinc sulfate, therefore, serves, as it were, as an indicator, inasmuch as the pure white precipitate will not be formed until the mercury is completely precipitated. Filter off the precipitated sulfides and wash with dilute ammonia. The filtrate contains all the hydrocyanic acid. Add to it an excess of silver nitrate, make acid with nitric acid, filter, and determine the weight of silver in the silver cyanide as described on p. 301.

Determination of Hydrocyanic Acid and Halogen Hydride in the Presence of One Another, according to Neubauer and Kerner[1]

Treat the solution with silver nitrate in the cold, add nitric acid to faintly acid reaction, and heat to coagulate the precipitate. Filter, dry at 130°, and in this way determine the total weight of the silver salts. Place a definite amount of the precipitate in a porcelain crucible, heat until it is completely melted, and reduce with zinc and sulfuric acid as described on p. 295. Dilute with water, filter off the metallic silver and paracyanogen, and determine the halogen in the filtrate according to pp. 291 *et seq.*

The above separation can be more satisfactorily effected by means of a volumetric process (see Chapter XVII).

THIOCYANIC ACID, HCNS. Mol. Wt. 59.08

Forms: $Cu_2(CNS)_2$, AgCNS, $BaSO_4$

1. Determination as Cuprous Thiocyanate, $Cu_2(CNS)_2$

To the solution of thiocyanate, which is neutral or slightly acid with hydrochloric or sulfuric acid, add 20–50 ml of a saturated solution of sulfurous acid, and copper sulfate solution with constant stirring until a slightly greenish tint is imparted to the liquid. After allowing to stand for a few hours, transfer the precipitate to a filtering crucible, wash with cold water containing sulfurous acid, then once with alcohol, and dry at 130° to constant weight.

2. Determination as Silver Thiocyanate, AgCNS

This excellent method for estimating thiocyanic acid is applicable only in the absence of the halogen acids or hydrocyanic acid.

Treat the dilute solution of the alkali thiocyanate in the cold with a slight excess of silver nitrate solution, which has been acidified with nitric acid. After stirring well, filter off the precipitate into a Munroe crucible, wash with water, then with a little alcohol, dry at 130°, and weigh.

3. Determination as Barium Sulfate

In the absence of all other compounds containing sulfur, thiocyanic acid can be determined with accuracy by oxidizing it and precipitating the sulfuric acid formed as barium sulfate. Bromine water is the most suitable oxidizing agent for this purpose. Treat the alkali thiocyanate

[1] *Ann. Chem. Pharm.*, 101, 311 (1857).

solution with an excess of bromine water, heat for 30–60 minutes on the water bath, acidify the solution with hydrochloric acid, precipitate the sulfuric acid by means of barium chloride, and weigh as barium sulfate (see " Sulfuric Acid ").

Determination of Thiocyanic and Hydrocyanic Acids in the Presence of One Another (Borchers)[1]

In one portion determine by volumetric titration the quantity of silver nitrate necessary to precipitate both the acids (see Chapter XVII, "Precipitation Analyses "), and in a second portion determine the weight of barium sulfate formed after the oxidation of the thiocyanic acid. From the latter weight compute the quantity of thiocyanic acid present and also the weight of silver nitrate that would be required to precipitate it. If this weight is subtracted from the weight of silver nitrate required to precipitate both the acids, the quantity of silver nitrate equivalent to the hydrocyanic acid present is obtained.

Determination of Thiocyanic Acid together with Halogen Hydrides (Volhard)

In one portion determine the thiocyanic acid as barium sulfate after oxidation. Heat a second portion in a closed tube with concentrated nitric acid and silver nitrate (Carius method,[2] p. 293), filter off and weigh the mixture of silver halides and change to silver chloride as described on p. 298. Fuse a third portion with sodium carbonate and potassium nitrate, dissolve the alkali salts in water, and determine the iodine as palladous iodide (see p. 297). From the data thus obtained, compute the relative quantities of the three halides (see p. 299).

FERROCYANIC ACID, H₄Fe(CN)₆.   Mol. Wt. 216.0

Form: Silver Cyanide, AgCN

The most accurate procedure for the analysis of complex cyanides is to determine the carbon and nitrogen by elementary analysis (which see).

Determination as Silver Cyanide (Rose-Finkener)

This method depends upon the fact that all salts of ferrocyanic acid on being heated with yellow mercuric oxide give up their cyanogen to

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[1] *Repertorium der anal. Chemie*, 1881, p. 130.

[2] Instead of using the Carius method, the halogens and thiocyanate may be precipitated by silver nitrate, filtered through a Gooch crucible, dried at 160°, and weighed.

the mercury, forming soluble mercuric cyanide, while the iron is changed to insoluble ferric hydroxide. Thus Prussian blue is decomposed as follows:

$$Fe_4[Fe(CN)_6]_3 + 9HgO + 9H_2O = 9Hg(CN)_2 + 4Fe(OH)_3 + 3Fe(OH)_2$$
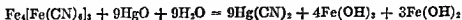
Treat a weighed amount of the substance with water and an excess of mercuric oxide. Boil until the blue color has completely disappeared, filter off the iron precipitate with the excess of mercuric oxide, and determine the cyanide in the filtrate according to p. 302.

On filtering off the insoluble oxides, at first a clear filtrate is obtained, but on washing some of the precipitate usually passes through the filter. By washing with a solution containing a dissolved salt, preferably mercuric nitrate, it is possible, however, to obtain a clear filtrate. Even then the operation is tedious, so that it is better to dilute the liquid containing the precipitate suspended in it to 100 ml, and use a filtered aliquot of 50 ml for the determination of the cyanide according to p. 302. A slight error is introduced because the volume of the precipitate is neglected, but it is largely compensated by adsorption errors.

Soluble ferrocyanides may be determined satisfactorily by titration with potassium permanganate (cf. Chapter XV, "Oxidation and Reduction Methods"). For the determination of the iron and other metals, heat the substance with concentrated sulfuric acid, dissolve the residue after evaporation in water, and analyze the solution in the usual way.

FERRICYANIC ACID, $H_3Fe(CN)_6$. Mol. Wt. 215.0

The ferricyanides are analyzed in the same way as the ferrocyanides.

HYPOCHLOROUS ACID, HClO. Mol. Wt. 52.47

Hypochlorous acid is always determined volumetrically and will be discussed in Chapter XV of this book, under "Oxidation Methods."

GROUP II OF ANIONS

NITROUS, HYDROSULFURIC, ACETIC, CYANIC, AND HYPOPHOSPHOROUS ACIDS

NITROUS ACID, HNO_2, Mol. Wt. 47.02

Nitrous acid is determined either volumetrically, gasometrically, or colorimetrically. The first two methods will be discussed in Parts II and III of the book.

Colorimetric Determination of Peter Griess

This method serves only for the determination of extremely small amounts of nitrous acid (e.g., in drinking waters), and depends upon the formation of intensely colored azo dyes.

Inasmuch as azo compounds are formed only when nitrous acid is present, they can all be used in testing for this acid, but the different substances do not prove equally sensitive as reagents. Thus in the production of triaminoazobenzene (Bismarck brown) not less than 0.02 mg of nitrous acid in a liter can be detected, whereas according to the following procedure 0.001 mg in a liter can be detected with certainty. To carry out the determination two solutions are necessary, one of sulfanilic acid and one of α-naphthylamine. Both substances are dissolved in acetic acid[1] and prepared according to the directions of Ilosvay[2] as follows:

1. Dissolve 0.5 g of sulfanilic acid in 150 ml of dilute acetic acid.

2. Boil 0.1 g of solid α-naphthylamine with 20 ml of water, pour off the colorless solution from the bluish violet residue, and add 150 ml of dilute acetic acid.

Mix these two solutions.[3] It is not necessary to protect the reagent from the action of light, but it is desirable to keep impure air away from it. As long as the solution remains colorless it can be used. If it comes in contact with nitrous acid, which is often present in the air, the re-

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[1] P. Griess used dilute sulfuric acid to set free the nitrous acid. Ilosvay showed that if acetic acid were used the reaction was much more sensitive.

[2] *Bull. chim.* [2] 2, 317.

[3] Lunge, *Z. angew. Chem.*, 1899, Heft 23.

agent becomes red and must be decolorized by shaking with zinc dust before using.

Besides the above reagent, it is necessary to prepare a solution of sodium nitrite of known strength. For this purpose add silver nitrate solution to a concentrated solution of commercial potassium nitrite, filter off the precipitated silver nitrite, and wash a few times with cold water. To obtain absolutely pure silver nitrite dissolve the precipitate in as little hot water as possible and quickly cool. Place the mass of crystals in a funnel provided with a platinum cone and, after draining off the mother liquor by suction, wash with a small amount of distilled water. Place the silver nitrite in a calcium chloride desiccator and allow to dry in the dark. As soon as it has become dry (shown by its having assumed a constant weight) dissolve exactly 0.4047 g in a liter flask with hot distilled water. Add 0.2–0.3 g of pure sodium chloride (i.e., a little more than the theoretical amount) to convert the silver nitrite into silver chloride and sodium nitrite. Cool, dilute the solution to exactly 1 l with pure water, shake well, and allow the precipitate to settle. After this, pipet off 100 ml of the clear liquid into a second liter flask and dilute up to the mark with water free from nitrous acid. One milliliter of this solution contains 0.01 mg N_2O_3.

Procedure. Place 50 ml of the water to be examined in a Nessler tube, add 5 ml of the reagent, and mix the contents of the cylinder with the aid of a stirrer. Place the cylinder in water heated to 70–80°. If as much as 0.001 mg of nitrous acid is present in a liter of the water tested, the red coloration will appear within 1 minute; with relatively larger amounts (e.g., as much as 1 mg per liter) the solution is simply colored yellow, unless a concentrated solution of naphthylamine is used. Meanwhile in three other Nessler tubes place respectively 0.1 ml, 0.5 ml, and 1 ml of the standard solution of sodium nitrite; dilute each with water up to the mark and treat with the reagent in the same way. As soon as a distinct red coloration is apparent, compare the colors with that produced by the water to be analyzed. If the color of the unknown water lies between two of the standards — e.g., between that produced with 0.1 and 0.5 ml of the standard — then prepare three more standards containing, say, 0.2, 0.3, and 0.4 ml of the known solution. When the color of the unknown solution is matched, then the water contains the same amount of nitrous acid as the standard.

If the water contains considerable nitrous acid (e.g., over 0.3 mg per liter), the red coloration will be so dark that the colorimetric determination cannot be performed with certainty. In this case dilute a definite volume of the water with distilled water and determine the nitrous acid present in this diluted water.

HYDROGEN SULFIDE (HYDROSULFURIC ACID), H₂S.   Mol. Wt. 34.08

**Forms: Barium Sulfate, BaSO₄, Hydrogen Sulfide, H₂S,
and colorimetrically**

There are four cases to be considered:

  I. The determination of free hydrogen sulfide.
 II. The determination of sulfur in sulfides soluble in water.
III. The determination of sulfur in sulfides insoluble in water but decomposable by dilute acids with evolution of hydrogen sulfide.
 IV. The determination of sulfur in insoluble sulfides.

I. Determination of Free Hydrogen Sulfide

(a) Determination of Hydrogen Sulfide in Gas Mixtures

If it is desired to know the percentage of hydrogen sulfide present in a mixture of gases, the analysis is best made volumetrically (see Chapter XV, " Iodimetry "), but it is possible to accomplish the same end by a gravimetric procedure.

Connect the source of the gas by means of rubber tubing with a ten-bulb Meyer absorption tube which contains a solution of ammoniacal hydrogen peroxide free from sulfuric acid. Connect the other end of the absorption tube with an aspirator, i.e., a large bottle of about 4- to 5-liter capacity filled with water and closed by means of a double-bored stopper. Through one hole of the stopper pass a right-angled glass tube which reaches just below the bottom of the stopper in the bottle and is connected at the other end with the absorption tube. Through the other hole in the stopper place a glass tube reaching to the bottom of the bottle. Likewise bend the upper end of this tube, and connect with a rubber tube to serve as a siphon; on the lower end of the rubber tube place a screwcock.

Before beginning the experiment, remove the air in the rubber tubing between the source of gas and the absorption tube by conducting the gas to be analyzed through it. When this is accomplished connect the tubing with the absorption tube. Now allow water to run slowly from the aspirator into a vessel graduated in liters; after 2 to 5 liters of the water have run out, close the aspirator by screwing up the cock on the siphon arm. Pour the contents of the absorption tube into a beaker, slowly heat to boiling, and keep at this temperature for 5–10 minutes. Evaporate the solution on the water bath to a small volume, add a little hydrochloric acid, filter the solution if necessary, and precipitate the sulfuric acid at a boiling temperature with a boiling solution

of barium chloride. After the precipitate has settled, filter it off, ignite wet in a crucible, and weigh as barium sulfate.

Both at the beginning and end of the experiment it is necessary to note the temperature of the room and the barometer reading. Use the mean of these readings for the calculation. Compute the amount of hydrogen sulfide present in the gas as follows:

The volume of water which has flowed out of the aspirator represents the volume of the gas that has been drawn through the apparatus less the amount absorbed by the ammoniacal hydrogen peroxide solution. Let V represent the volume of water in liters which has flowed from the aspirator and p the weight of barium sulfate found.

Since one gram molecule of barium sulfate corresponds to one gram molecule of hydrogen sulfide and the latter assumes at $0°$ and 760 mm pressure a volume of 22.16 liters,[1] we have:

$$V_1 = \frac{22.16 \cdot p}{BaSO_4} = \text{the volume of the hydrogen sulfide absorbed in liters.}$$

Now the volume (V) of the gas that passed through the apparatus was at $t°$ and B mm pressure and was saturated with water vapor; whereas V_1 refers to the dry gas at $0°$ C and 760 mm pressure. It is necessary, therefore, to reduce V to $0°$ C and 760 mm pressure.

$$V_0 = \frac{V \cdot (B - w)273}{760(273 + t)}$$

where w is the tension of aqueous vapor at $t°$.

The volume of the gas drawn through the apparatus is then:

$$V_0 + V_1$$

and we have: $\dfrac{V_1 \cdot 100}{V_0 + V_1} = $ the percentage by volume of hydrogen sulfide present.

(b) Determination of Hydrogen Sulfide Present in Solution

By means of a pipet measure out a definite volume of the solution and allow it to run into ammoniacal hydrogen peroxide while constantly stirring with the pipet. Heat to boiling, acidify with hydrochloric acid, and determine the amount of sulfate by precipitation with barium chloride.

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[1] According to Leduc, *Compt. rend.*, **125**, 571 (1897), the density of H₂S (referred to air = 1) is 1.1895, from which the gram-molecular volume is computed as 22.159.

II. Determination of Sulfur in Sulfides Soluble in Water

(α) Treat the solution with an excess of ammoniacal hydrogen peroxide water, slowly heat to boiling, and keep at this temperature until the excess of the reagent is destroyed. Then precipitate the sulfuric acid with barium chloride and weigh as barium sulfate.

(β) Treat the solution with bromine water until a permanent brown color is obtained, heat, make acid with hydrochloric acid, and determine the sulfuric acid as barium sulfate.

If the solution contains thiosulfate, sulfide, and sulfate, as it is likely to after standing in the air for some time, precipitate the sulfide sulfur by means of cadmium acetate and determine the sulfur in the precipitate as under III, or oxidize the cadmium sulfide with either bromine water or fuming nitric acid, and determine the sulfuric acid formed as barium sulfate.

The determination of thiosulfate, sulfide, and sulfite sulfur will be discussed in Chapter XV under "Iodimetry."

III. The Determination of Sulfur in Sulfides Soluble in Dilute Acids

Principle. The hydrogen sulfide is evolved by treatment of the sulfide with dilute acid and absorbed in ammoniacal hydrogen peroxide solution as under I; or the hydrogen sulfide is absorbed in caustic soda solution and the sodium sulfide formed analyzed according to II; or finally the gas may be absorbed in a weighed tube containing pumice soaked with copper sulfate solution, the gain in weight representing the amount of gas absorbed.

Evolution and Absorption of the Hydrogen Sulfide

Of sulfides rich in sulfur take 0.25–0.50 g of the substance for analysis, and of sulfides containing less sulfur use a correspondingly larger amount. Place the substance in an Erlenmeyer flask (K, Fig. 42), break the connection between the flask and the receiver, and expel the air from K by conducting hydrogen gas through the delivery tube and out through the open stopcock of T. After a rapid current of hydrogen has passed through the apparatus for about 5 minutes, partly fill the receivers V and P with an ammoniacal solution of hydrogen peroxide[1] (about

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[1] Instead of hydrogen peroxide, the receivers can contain 100 ml of 25 per cent sodium hydroxide solution. After the decomposition is complete transfer the contents of the receiver to a beaker, add 30–50 ml of bromine water, make the solution acid with hydrochloric acid, and boil while passing carbon dioxide through it until the excess of bromine is completely expelled. Then precipitate the sulfuric acid formed with a hot solution of barium chloride. Instead of oxidizing the sodium sulfide to sodium sulfate it can be titrated with iodine (cf. Chapter XV, "Iodimetry").

3–4 per cent H_2O_2); place about 100 ml of the solution in V and 10–20 ml in P.

Now connect the receiver, V, with the delivery tube from the evolution flask K, and conduct hydrogen from T through the whole appa-
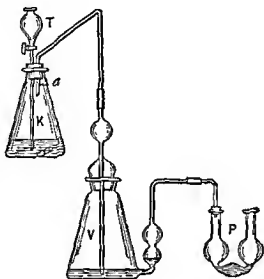
Fig. 42.

ratus for 5 minutes more in order to remove as much as possible of the air from the receivers. After this, introduce about 20 ml of boiled water into K through T so that the substance is entirely covered, then slowly add 6 N hydrochloric acid to the contents of the flask and promote the decomposition by warming somewhat. When the evolution of the gas has ceased, heat the contents of K to gentle boiling and pass a slow current of hydrogen[1] through the apparatus from T for 20 minutes; then remove the flame and continue the current of hydrogen for 15 minutes longer. At the end of this time, the hydrogen sulfide will be completely driven over into V.[2]

---

[1] Prepare the hydrogen from zinc and sulfuric acid in a Kipp generator. Wash the gas first with an alkaline solution of lead acetate to remove traces of hydrogen sulfide and then with water.

[2] By the absorption of the hydrogen sulfide in the ammoniacal solution of hydrogen peroxide the latter is always colored somewhat yellow from the formation of a little ammonium disulfide. This yellow color can be distinctly seen in the delivery tube, where it dips into the solution in the receiver and later disappears owing to further oxidation:

$$(NH_4)_2S_2 \rightarrow (NH_4)_2S_2O_3 \rightarrow (NH_4)_2SO_3 \rightarrow (NH_4)_2SO_4$$
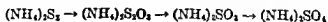
When the color can no longer be detected, it is a sign that the greater part of the hydrogen sulfide has been driven over.

Wash the contents of the two receivers into a beaker and slowly heat to boiling in order to effect the complete oxidation of the thiosulfuric and sulfurous acids and to expel the excess of the hydrogen peroxide. Finally make the solution acid with hydrochloric acid and determine the sulfuric acid as barium sulfate.

This method yields excellent results and can be applied to the

Determination of Sulfur in Iron and Steel

Sulfur occurs in irons and steels chiefly as sulfide of iron, manganese, or titanium and represents impurity or, in other words, enclosed slag. Manganese sulfide is the most commonly occurring form, and iron sulfide is formed only when more sulfur is present than there is manganese to combine with it. The occurrence of titanium sulfide is rare.

The effect of sulfur present as iron sulfide is to make the metal "red short," i.e., brittle at the forging temperature. The effect is overcome by the addition of manganese, but sometimes the manganese sulfide becomes rolled out into filaments and these are brittle and cause weakness. Breaks in the metal often start where there is some manganese sulfide; this compound is easily identified in etched specimens by its characteristic dove color under the microscope. The maximum permissible sulfur content is usually specified among the requirements of a given kind of steel. Most steels contain less than 0.05 per cent, but in some samples of stainless steel it may run as high as 0.45 per cent.

Sulfur can be determined colorimetrically by treating the steel with acid and causing the escaping gases to pass through a cloth which has been moistened with cadmium acetate solution. The estimation of the sulfur content is then based on a comparison of the tint produced with tints produced similarly with steels containing known quantities of sulfur.

In ordinary routine work, sulfur in steel is usually determined by the so-called *evolution method*. (See Chapter XV.) The sample is treated with hydrochloric acid, and the escaping hydrogen sulfide is collected in some suitable absorbent, such as an ammoniacal solution of zinc sulfate or of cadmium chloride. The hydrogen sulfide is liberated again by treatment with acid and oxidized at once to free sulfur either directly by adding a measured volume of iodine, or indirectly by adding a measured volume of potassium permanganate or potassium iodate solution together with an excess of potassium iodide, whereby a known quantity of iodine is liberated. Finally the excess iodine is titrated with sodium thiosulfate.

When great accuracy is desired, it is best to oxidize the sulfur to sulfate and precipitate this as barium sulfate which can be ignited and

weighed. Much has been written about the difficulty of obtaining pure precipitates of barium sulfate, especially in the presence of considerable ferric salt. To overcome this difficulty: (1) It has been proposed to remove the greater part of the iron as ferric chloride by shaking the HCl solution with ether. This method gives excellent results, but the procedure is rather long and work with ether is not altogether pleasant. (2) Meineke recommended treating the sample of steel with a slightly acid solution of cupric and potassium chlorides. This leaves the sulfur in the residue which is filtered off, oxidized by HNO_3 and $KClO_3$, and eventually precipitated as $BaSO_4$. (3) Bamber, on the other hand, evaporated the HNO_3 solution of the steel to dryness after adding some alkali salt, and then, by ignition over an alcohol flame, the ferric nitrate was decomposed and made insoluble in water while the sulfur was left as soluble alkali sulfate. Then, after the addition of acid, the sulfate was determined as barium sulfate in the usual way.

In this book directions will be given for a simple method of carrying out the gravimetric determination, and in Chapter XV the evolution method will be described.

Procedure. Dissolve 4.57 g of steel $(100 \times S)/(3 \times BaSO_4)$ by heating carefully with 50 ml of concentrated HNO_3. If the sample dissolves very slowly, add a little concentrated HCl dropwise at intervals. To the solution add 0.5 g of Na_2CO_3, evaporate carefully to dryness, and bake for 15 minutes on the hot plate. Cool, add 30 ml of concentrated HCl, and repeat the evaporation and baking. Now add 30 ml of concentrated HCl and evaporate to a sirup. Add 5 ml more of HCl, 20 ml of water, and 5 g of 20–30 mesh zinc, free from sulfur. This serves to reduce the iron to ferrous salt which does not interfere as much as $FeCl_3$ does with the precipitation of all SO_4^{--} as pure $BaSO_4$. Heat on the water bath until all the ferric ions are reduced and the evolution of hydrogen has nearly ceased. Filter and wash with about 75 ml of 0.25 N HCl, added in small portions. Heat to about 70°, and add 10 ml of 10 per cent barium chloride solution. Allow to stand over night. Filter through an ashless filter; wash 6 times with hot N HCl and then with hot water until free from chloride. Ignite and weigh the $BaSO_4$. Run a blank on all the reagents going through all the above operations in exactly the same way. To find the percentage of sulfur, multiply the weight of the precipitate of $BaSO_4$ in grams by 3.

IV. Determination of Sulfur in Insoluble Sulfides

For this analysis the sulfur is either oxidized to sulfuric acid and determined as barium sulfate, or the sulfide is converted into a soluble sulfide which is analyzed as described above.

The oxidation of the sulfide can take place:

A. *In the Dry Way.*

B. *In the Wet Way.*

A. OXIDATION IN THE DRY WAY

Sodium Peroxide Method[1]

Procedure. Mix 0.5 g of pyrite with 5 g of pure sodium peroxide and 4 g of sodium carbonate in a nickel or iron crucible. Cut an opening in a piece of asbestos board (at least 4 in. square) sufficiently large to allow two-thirds of the crucible to project below the asbestos. The purpose of this shield is to keep the products formed by the combustion of the gas from reaching the mouth of the crucible. Heat the contents of the crucible gently for 10 minutes so that the mass softens and bakes together, and then raise the temperature until the crucible is exposed to the full heat of the Tirrill burner for 20 minutes.

Allow the contents of the crucible to cool and place in a small beaker with 150 ml of hot water. When the sodium salts are entirely dissolved, remove the crucible and add 5 ml of a saturated solution of bromine in concentrated hydrochloric acid. The purpose of the bromine is to make sure that the oxidation of the sulfur is complete.[2] It is necessary to add acid, because otherwise the hot sodium hydroxide solution is likely to destroy the filter paper. After heating to boiling, filter the solution and wash the residue of ferric hydroxide free from sulfate.

Carefully neutralize the filtrate with 6 N hydrochloric acid, and add 2 ml in excess. Heat the solution till all the bromine is expelled, dilute to 350 ml, heat to boiling, and precipitate with 24 ml of normal barium chloride solution which is diluted to 100 ml and added slowly while stirring vigorously. Filter, wash, ignite, and weigh the barium sulfate precipitate in the usual way (see Chapter XI).

B. OXIDATION IN THE WET WAY

For this purpose aqua regia, fuming nitric acid, bromine, hydrochloric acid and potassium chlorate and, in some cases, ammoniacal hydrogen peroxide have been proposed.

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[1] W. Hempel, *Z. anorg Chem.*, **3**, 193 (1893); J. Clark, *J. Chem. Soc.*, **63**, 1079 (1893); Höhnel, *Arch. Pharm.*, **232**, 222; C. Glaser, *Chem.-Ztg.*, **18**, 1448; Fournier, *Rev. gén. chim.*, 1903, 77; List, *Z. angew. Chem.*, 1903, 414.

[2] A black residue may denote ferrous sulfide or nickelic oxide. It may be tested for sulfur by dissolving in hydrochloric acid and bromine and adding barium chloride to the diluted solution.

Aqua regia is most frequently used in practice and in the proportion first recommended by J. Lefort,[1] viz., 3 volumes of concentrated nitric acid, d 1.4, and 1 volume of concentrated hydrochloric acid, d 1.2. As an example we will cite the

Sulfur in Pyrite. Method of G. Lunge

The sample should be finely ground, but it must be borne in mind that rapid grinding in the air may generate enough heat to cause the oxidation of some sulfur so that an appreciable amount escapes as dioxide. Of the fine powder, treat 0.5 g with 10 ml of a mixture consisting of 3 parts of 16 N nitric acid, and 1 part 12 N hydrochloric acid, in a 300-ml beaker which is covered with a watch glass. At first allow the acid to act upon the pyrite in the cold, but finish by heating upon the water bath. If sulfur separates, oxidize it with a very little powdered potassium chlorate. Transfer the solution to a porcelain evaporating dish and evaporate to dryness on the water bath. Treat the residue with 5 ml of 12 N hydrochloric acid and again evaporate to dryness. Moisten the dry mass now with 1 ml of 12 N hydrochloric acid and 100 ml of hot water, filter through a small filter, and wash the residue first with cold water and then with hot water. To the hot filtrate, if not more than 150 ml in volume, add ammonia till the odor persists and then 30 ml of 3 N ammonium hydroxide in excess to prevent the formation of any basic ferric sulfate. Keep at about 70° for 15 minutes. Filter off the ferric hydroxide precipitate and wash with hot water, each time churning up the precipitate, until a volume of about 400 ml is reached. Neutralize the filtrate with hydrochloric acid, using methyl orange as indicator, and add 1 ml of 12 N hydrochloric acid in excess. Heat just to boiling, and add 100 ml of boiling-hot 0.2 N barium chloride solution while stirring vigorously.

Wash the barium sulfate precipitate 3 times by decantation with boiling water, then transfer to a filter and wash free from chlorides, ignite, and weigh.

To test the ammonia precipitate for sulfur, transfer it from the filter into a beaker by means of a stream of water from the wash bottle and dissolve it by the addition of as little hydrochloric acid as possible To the resulting solution add an excess of ammonia, filter, and test the filtrate and washings as in the main analysis. Should any barium sulfate be obtained in this way, it should be filtered off and weighed with the main part of the barium sulfate precipitate.

Remark: It is still better to filter the precipitate through a filtering crucible After washing, dry the precipitate as much as possible by suction, place the cru-

[1] *J. pharm. chim*, [IV] 9, 99, and *Z. anal. Chem.*, 9, 81.

cible within a larger porcelain or platinum crucible, heat gently, cool, and weigh.

The above method gives excellent results, which as a rule agree closely with those obtained by the preceding method. If the pyrite, however, contained barium or any considerable amount of lead, some sulfate will always remain undissolved with the gangue. In such cases the Lunge method will give lower results but on the other hand it represents more nearly the quantity of sulfur in the pyrite which is available for the manufacture of sulfuric acid. In spite of the strong oxidizing power of the above mixture of nitric and hydrochloric acids, it is not sufficient to permit the determination of sulfur in roasted pyrite, on account of the danger of losing some sulfur as hydrogen sulfide. Such products should be fused with sodium carbonate and peroxide as previously described.

In carrying out the Lunge method, often a little sulfur separates in dissolving the sample. It has been recommended that this sulfur be dissolved by adding potassium chlorate, but when this is done the results are likely to be high. To overcome this difficulty, Allen and Bishop recommend dissolving the pyrite in a mixture of bromine and carbon tetrachloride. The latter dissolves any sulfur that is liberated, and the dissolved sulfur is easy to oxidize.

Determination of Sulfur in Pyrite. Method of Allen and Bishop[1]

Weigh 0.5495 g of sample, ground to pass an 80-mesh sieve, into a tall beaker of 300 to 400-ml capacity, and add 6–8 ml of a solution of 2 volumes of liquid bromine in 3 volumes of pure carbon tetrachloride (free from sulfur). Cover the beaker and allow to stand 15 minutes at room temperature with occasional gentle shaking. Add 10 ml of concentrated nitric acid and digest in the same way for another 15 minutes. Heat at a temperature below 100° until all action has ceased and most of the excess bromine has been expelled. Raise the cover glass and evaporate to dryness. Cover the residue with 10 ml of concentrated hydrochloric acid, again evaporate to dryness, and heat the contents of the covered beaker for at least 30 minutes at 100°.

Moisten the residue with 4 ml of concentrated hydrochloric acid and after 5 minutes dilute with 50 ml of hot water, washing the cover glass and the sides of the beaker. Heat until all the ferric salt is dissolved, and allow to cool for 3 minutes.

Reduce the iron by adding 0.1 g of powdered aluminum, shaking the contents of the covered beaker to bring the metal in contact with all parts of the solution. Sufficient aluminum should be added to reduce all the iron to the ferrous condition, but any considerable excess is to be avoided.

When the reduction of the iron is complete, as shown by the solution becoming nearly colorless, and the solution has cooled sufficiently so that there is no noticeable "misting" in the beaker, filter off the silica and the excess aluminum and wash with water until free from chloride. Dilute

[1] J. Ind. Eng. Chem., 11, 46 (1919).

with cold water to a volume of 650 ml, add 5 ml of 6 N hydrochloric acid, and stir thoroughly. To the cold solution slowly introduce, while stirring, 50 ml of cold 5 per cent barium chloride solution in single drops, at the rate of about 5 ml per minute. Allow the precipitate of barium sulfate to settle at least 2 hours and preferably over night. Filter, wash with cold water till free from chloride, dry, ignite, and weigh in the usual manner. The weight of the precipitate multiplied by 25 gives the percentage of sulfur.

A modification of the Allen and Bishop method, proposed by Lundell and Scherrer of the National Bureau of Standards, has been found excellent for determining sulfur in stibnite, Sb_2S_3 Digest 0 5495 g of sample in a porcelain casserole with 10 ml of 10 per cent bromine in CCl_4. After 15 minutes add 5 ml of liquid bromine slowly and with frequent shaking. Allow to stand for at least 30 minutes with occasional shaking, add 15 ml of concentrated HNO_3, and allow to stand at least 15 minutes. Now add 15 ml of concentrated HCl and allow to stand 15 minutes more. Heat slowly to drive off CCl_4, and then evaporate to sirupy consistency but do not allow to dry Add 10 ml more of HCl and again evaporate to a sirup but not to dryness; this serves to remove all HNO_3 Now add 20 ml of concentrated HCl and heat until all soluble matter is dissolved. Transfer to a 500-ml Erlenmeyer flask but keep the volume under 100 ml Add 5 g of ingot iron drillings, let stand an hour, filter, and determine the sulfuric acid in the filtrate as in the analysis of pyrite after the reduction with aluminum.

Determination of Sulfur in Coal, Eschka Method[1]

If sulfur compounds are heated with a mixture of magnesium oxide and sodium carbonate, all the sulfur can be converted into water-soluble sulfate. It is generally assumed that air is the oxidizing agent and the heating is usually accomplished in an open dish Recently, however, the use of a porcelain or platinum crucible has been advocated and the results appear to be equally good, which indicates that the oxidation of the sulfur may be accomplished as a result of the reduction of the carbonate. The magnesium oxide prevents the mass from fusing and apparently also catalyzes the oxidation which, however, is not so rapid as when an oxidizing flux is used.

Prepare Eschka's ignition mixture by mixing 2 parts of light calcined magnesium oxide with 1 part of anhydrous sodium carbonate, both free from sulfur. Mix 1 g of 60-mesh sample with 3 g of the Eschka mixture on a sheet of glazed paper. For coals high in volatile matter or sulfur add 0.5 g NH_4NO_3 to the Eschka mixture. Transfer to a porcelain, silica, or platinum dish, or to a spacious crucible, and cover with about 1 g of the Eschka mixture.

Heat slowly with an alcohol flame until most of the volatile matter has been driven off, then gradually raise the temperature and heat with the full flame of the burner for 30 minutes or more, stirring occasionally, until all the black particles have been oxidized.

[1] Chem. News, 21, 261 (1870)

After the ignition, rinse the material into a 200-ml beaker, add 100 ml of hot water, and digest on the steam bath for 30 minutes with occasional stirring. Filter and wash the insoluble residue thoroughly with hot water. The filtrate and washings should total about 250 ml. Add 20 ml of saturated bromine water, stir, make slightly acid with hydrochloric acid, and boil till the excess bromine is removed and the solution is colorless. To the boiling solution add dilute barium chloride solution (20 ml of a 5 per cent solution) and allow to stand at least 1 hour before filtering. Ignite and weigh the barium sulfate.

C. HYDROGEN SULFIDE FROM INSOLUBLE SULFIDES

The Iron Method[1]

In 1881, M. Gröger showed that by heating 0.3–0.5 g of pyrite with 3 g of pure iron powder out of contact with the air the pyrite is quantitatively changed into ferrous sulfide

$$FeS_2 + Fe = 2FeS$$

from which all the sulfur will be given off as hydrogen sulfide on treatment with hydrochloric acid. The method is suitable for the analysis not only of pyrite but also of all insoluble sulfides.

Remark. Commercial iron powder always contains a small amount of sulfur, so that a blank experiment must be made with a weighed amount of the powder, and the same quantity of iron used for the experiment proper. Subtract the amount of sulfur found to be present in the iron from the amount found in the analysis

It is not possible by this method to distinguish between the sulfur present in insoluble sulfides as sulfide and that present as sulfate (barium sulfate). If the amount of sulfate present is small, it is completely reduced to sulfide; if a large amount of sulfate is present, it is often only partially reduced. As the amount of barium sulfate[2] present in insoluble sulfides is usually small, however, this method serves for the determination of practically all the sulfur.

The Tin Method[3]

Principle. Almost all insoluble sulfides on being treated with metallic tin and concentrated hydrochloric acid give off their sulfur as hydrogen sulfide. Harding,[4] who first studied this method, used tin and hydrobromic acid.

Procedure. In the evolution tube (Fig. 43), which is 20 cm long and 2.5 cm wide, place a layer of finely powdered tin (*g*) about 0.5 cm thick. Upon this place the substance enclosed in tinfoil (*s*) and then a

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[1] *Ber.*, **24**, 1937 (1891).

[2] Only barium sulfate is reduced with difficulty; the sulfates of the heavy metals are easily reduced.

[3] *Ber.*, **25**, 2377.

[4] *Ber.*, **14**, 2085.

layer of granulated tin (Z) about 6 cm deep. Pass a current of pure hydrogen through the apparatus for about 5 minutes, after which close the stopcock and connect the tube with the receivers P and V, as shown in the figure. The flask V contains an ammoniacal solution of bydrogen peroxide, but P contains 2-3 ml of water to remove any stannous chloride that may be carried over with the gas. Add concentrated hydrochloric acid through the dropping funnel until the tin is at the most half covered with the acid. Heat the contents of the tube slightly, preferably by placing it in a small paraffin bath. The capsule of tin soon dissolves, and the substance is seen to be floating in the acid. It dissolves after about 15 minutes, and the acid becomes perfectly clear. Continue beating until no more yellow coloration can be detected in the delivery tube which dips into the receiver V. Then add more acid to the contents of the tube, until the tin is completely covered, and heat for half an hour longer, meanwhile heating the contents of P to boiling and passing a current of hydrogen through

Fig. 43.

a. By this means all the sulfur[1] will be driven over into V and there held in solution as ammonium sulfate and analyzed as described on p. 316.
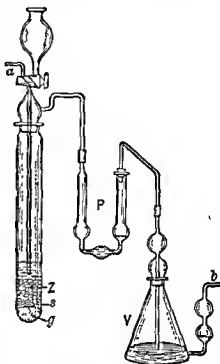
Remark. This method affords an accurate means for determining the sulfur present in insoluble sulfides as sulfide in the presence of sulfate   Thus the amount of pyrite in clay-slate that contains gypsum can be determined by this method, although usually the treatment with aqua regia or fusion with soda and niter is used. By these last two methods, however, the *total* sulfur is determined.   More accurate values for the *pyrite* present may be obtained by decomposition in a current of chlorine, in which case only the sulfide sulfur is determined.

Finally, it may be mentioned that arsenic sulfide may be decomposed by the above method, although a longer time is required than with pyrite, copper, chalcopyrite, galena, cinnabar, etc.   Arsenopyrite, on the other hand, is either unacted upon or only decomposed with difficulty, while the iron method effects the decomposition with ease.

[1] With large amounts of sulfur, one receiver is often insufficient   In such cases connect the tube b with a Péligot tube containing ammoniacal hydrogen peroxide as shown in Fig. 42, p 311

Determination of Sulfur in Non-Electrolytes

To determine the amount of sulfur present in organic compounds, it is oxidized to sulfuric acid and determined as barium sulfate.

The oxidation is effected:

(a) *In the Wet Way.*
(b) *In the Dry Way.*

(a) Oxidation in the Wet Way (Carius)

This operation is conducted in precisely the same manner as was described on p. 293 for the determination of halogens, except that no silver nitrate is added to the contents of the tube. After the closed tube has been heated and opened, transfer its contents to a beaker, add hydrochloric acid, and evaporate to a small volume in order to remove the nitric acid; dilute with water to a volume of about 200 ml, precipitate hot with a boiling solution of barium chloride, and weigh as barium sulfate.

(b) Oxidation in the Dry Way (Liebig)

Melt a mixture of 8 parts of potassium hydroxide (free from sulfate) and 1 part of potassium nitrate in a large silver crucible with the addition of a little water. After cooling, add a weighed amount of the substance and heat the contents of the crucible again very gradually, frequently stirring the mixture with a silver wire until the organic substance is completely decomposed. Cool, dissolve the melt in water, make acid with hydrochloric acid, and precipitate the sulfuric acid formed.

This method is particularly suited for the determination of sulfur present in difficultly volatile substances, e.g., in wood cements.

ACETIC ACID, $CH_3 \cdot COOH$. Mol. Wt. 60.05

Free acetic acid is always determined volumetrically. For the analysis of acetates, the substance is heated with phosphoric acid when the free acetic acid distils over and is then titrated (cf. Chapter XV, "Acidimetry"). The carbon and hydrogen of the acetate can be determined by elementary analysis (which see).

CYANIC ACID, HOCN. Mol. Wt. 43.03

The only method for examining cyanates consists in determining the amount of carbon and nitrogen present by a combustion (see "Elementary Analysis").

Determination of Cyanic Acid, Hydrocyanic Acid, and Carbonic Acid in a Mixture of Their Potassium Salts

In one portion of the substance determine the carbonic acid by adding calcium chloride to the ammoniacal solution and weighing the ignited precipitate as calcium oxide.

In a second portion determine the cyanogen of the cyanide as silver cyanide by treating the aqueous solution with an excess of silver nitrate, acidifying with nitric acid, and determining the weight of the silver cyanide as described on p. 301.

In a third portion determine the potassium by evaporating with sulfuric acid and weighing the residue of potassium sulfate as described on p. 269. If from the total amount of potassium present the amount present as potassium carbonate and potassium cyanide is deducted, the difference gives the amount of potassium combined with the cyanic acid.

HYPOPHOSPHOROUS ACID, H_3PO_2. Mol. Wt. 66.00

Forms: Mercurous Chloride, Hg_2Cl_2; Magnesium Pyrophosphate, $Mg_2P_2O_7$

(a) Determination as Mercurous Chloride

Treat the solution of the salt, which is slightly acid with hydrochloric acid, with an excess of mercuric chloride; by this means insoluble mercurous chloride is precipitated. After allowing to stand for 24 hours in a warm, dark place filter off the precipitate through a Gooch crucible, wash with water, dry at 110°, and from the weight of the mercurous chloride calculate the amount of hypophosphite present on the basis of the following reaction:

$$H_3PO_2 + 2H_2O + 4HgCl_2 = 2Hg_2Cl_2 + 4HCl + H_3PO_4$$
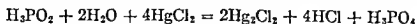
(b) Determination as Magnesium Pyrophosphate

First convert the hypophosphorous acid into phosphoric acid by adding 5 ml of concentrated nitric acid to the aqueous solution of 0.5–1 g of the substance in about 100 ml of water,[1] evaporating on the water bath to a small volume, adding a few drops of fuming nitric acid, and again heating. After this, precipitate the phosphoric acid by magnesia mixture and ammonia and weigh the precipitate as magnesium pyrophosphate as described under " Phosphoric Acid " in Chapter IX.

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[1] If the hypophosphite were at once treated with nitric acid, metaphosphoric acid would be obtained; by the addition of water the ortho salt is formed.

CHAPTER VIII

GROUP III OF ANIONS

SULFUROUS, SELENIOUS, TELLUROUS, PHOSPHOROUS, CARBONIC,
OXALIC, IODIC, BORIC, MOLYBDIC, TARTARIC, AND
META- AND PYROPHOSPHORIC ACIDS

SULFUROUS ACID, H_2SO_3.   Mol. Wt. 82.08

Form: Barium Sulfate, $BaSO_4$

The sulfite, or free sulfurous acid, is first oxidized to sulfuric acid and
then precipitated with barium chloride.   The oxidation can be accomplished by means of chlorine, bromine, hydrogen peroxide, or potassium
percarbonate.

Oxidation with Chlorine or Bromine

Allow chlorine water or bromine water to flow gradually into the
aqueous solution of sulfurous acid, or of a sulfite; after the oxidation is
complete, expel the excess of the reagent by boiling and precipitate the
sulfuric acid with barium chloride.

Oxidation with Hydrogen Peroxide[1]

Treat the solution of sulfurous acid or of a sulfite with an excess of
ammoniacal hydrogen peroxide, heat to boiling to remove the excess of
the peroxide, make acid with hydrochloric acid, and precipitate with
barium chloride.

With potassium percarbonate a similar procedure is used.   Treat
the cold alkaline solution of the sulfite with solid potassium percarbonate, heat gently, and gradually raise the temperature till the boiling point is reached.   Then make acid with hydrochloric acid and
precipitate with barium chloride.

Sulfurous acid may be determined very accurately by a volumetric
analysis (cf. Chapter XV, " Iodimetry ").

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[1] The hydrogen peroxide should always be tested to see if it contains sulfuric
acid; if it is found to be present, determine the amount and afterward use an accurately measured quantity for the oxidation.   Deduct the amount of sulfuric acid
from the peroxide from the total value found in the analysis.

Selenious and Tellurous Acids

The analysis of these acids was discussed under "Selenium" and "Tellurium."

PHOSPHOROUS ACID, H_3PO_3. Mol. Wt. 82.00

Forms: Mercurous Chloride, Hg_2Cl_2, and Magnesium Pyrophosphate, $Mg_2P_2O_7$

This determination is effected exactly like that of hypophosphorous acid (cf. p. 321).

Here, however, it is to be noted that 1 mole of Hg_2Cl_2 corresponds to 1 mole of H_3PO_3:

$$H_3PO_3 + 2HgCl_2 + H_2O = H_3PO_4 + 2HCl + Hg_2Cl_2$$
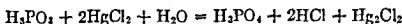
Determination of Phosphorous and Hypophosphorous Acids

In this case an indirect analysis must be made. After oxidizing one portion of the substance to phosphoric acid, determine the total phosphorus as magnesium pyrophosphate; allow mercuric chloride to act upon a second portion and determine the weight of mercurous chloride formed. From these data the amount of each acid present can be calculated as follows:

Assume that a solution containing the two acids is being analyzed. Let x denote the weight of hypophosphorous acid present in V ml of the solution.

Let m, n, o, and v represent the following chemical factors:

$$m = \frac{Mg_2P_2O_7}{2H_3PO_2} = 1.686 \qquad n = \frac{Mg_2P_2O_7}{2H_3PO_3} = 1.357$$

$$o = \frac{2Hg_2Cl_2}{H_3PO_2} = 14.30 \qquad v = \frac{Hg_2Cl_2}{H_3PO_3} = 5.757$$

Then ox is the weight of mercurous chloride produced from the hypophosphorous acid, and mx is the weight of magnesium pyrophosphate equivalent to the hypophosphorous acid. Further, let y represent the weight of phosphorous acid present in the same volume of the solution; then vy is the corresponding amount of mercurous chloride, and ny that of magnesium pyrophosphate. The total amount of the mercurous chloride is q, and the total amount of magnesium pyrophosphate is p. Then

$$mx + ny = p$$
$$ox + vy = q$$

from which it follows that

$$x = q\,\frac{n}{on - mv} - p\,\frac{v}{on - mv} = 0.1401q - 0.5943p$$

and

$$y = p\,\frac{o}{on - mv} - q\,\frac{m}{on - mv} = 1.477p - 0.1744q$$

CARBONIC ACID, H_2CO_3.   Mol. Wt. 62.03

Carbonic acid is determined gravimetrically as CO_2; it can also be determined by measuring the volume of the gas or by titrating with an acid to determine the amount required to decompose a carbonate.

(a) Determination in the Dry Way

Weigh out 1-2 g of the substance into a porcelain boat, and push the boat into the middle of a horizontally held glass tube, about 20 cm long and 1–1.5 cm wide, and made of difficultly fusible glass. Both ends of the tube should be provided with calcium chloride tubes connected with it by means of tightly fitting rubber stoppers. Through one of the calcium chloride tubes pass a slow stream of air (free from carbon dioxide)[1] and connect the other with two weighed soda-lime or Ascarite tubes (cf. pp. 325, 344). Heat the substance gradually until it glows strongly, meanwhile passing a slow but steady current of air through the apparatus. When there is no further heat effect to be detected in the absorption tubes, allow the substance to cool in the current of air and subsequently weigh the tubes. The increase of weight represents the amount of carbon dioxide.

Remark. This method can be employed for the analysis of all carbonates with the exception of those of barium and the alkalies,[2] though, of course, no other volatile acid can be present at the same time. Water is kept back by the calcium chloride tubes and the carbon dioxide in the air is removed by the same absorbent as that used in the weighed tubes.

(b) Determination in the Wet Way

The apparatus for this determination is shown in Fig. 44. The decomposition flask F should have a capacity of about 250 ml; a wide-mouthed flask such as is used for Soxhlet extractions is also suitable. The tube T of 8-mm diameter and about 30 cm long acts as an efficient air condenser. If a hole is blown at E, the flow of

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[1] The air is previously passed through two soda-lime or Ascarite tubes.

[2] Even the carbonates of the alkalies and of barium can be analyzed in this way if they are mixed with potassium dichromate.

gas from the decomposition flask is not impeded by condensed moisture during the experiment, but this is not very important.

A and *B* are Erlenmeyer flasks of 100- to 125-ml capacity. *A* is empty, but *B* contains enough concentrated sulfuric acid to act as a bubble counter and to show whether the apparatus is tight. *C* is a Midvale absorption tube containing some drying agent such as *Dehydrite*, Mg(ClO$_4$)$_2$·3H$_2$O, between cotton plugs, and *D* is a similar tube containing Ascarite (asbestos impregnated with NaOH) with cotton at the top and bottom. Instead of *Dehydrite*, calcium chloride (of the grade marked "for drying tubes"), *Anhydrone*, Mg(ClO$_4$)$_2$, or *Desiclora*, Ba(ClO$_4$)$_2$, can be used. The tube *H* should contain Ascarite to remove CO$_2$ from the air.
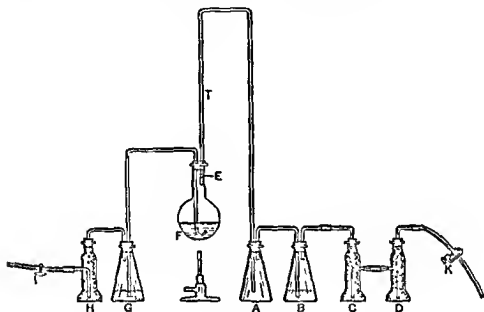
Fig. 41.

By means of *K*, a small screw clamp on rubber tubing which is connected with suction, the rate of flow of gas through the apparatus can be regulated. *G* is another 100- to 125-ml Erlenmeyer flask which is, at the start, about half full of normal HCl. *H* contains Ascarite. In the drawing a Midvale tube is shown at *H*, but a U-tube or any absorbing tower can be used equally well. The glass tubing that connects *F* and *G* should reach nearly to the bottom of each flask; it is well to make the tube a little narrower where it ends at the bottom of the flask *F* and to have the tip turned upward.

For decomposing the carbonate, sulfuric acid, hydrochloric acid, phosphoric acid, perchloric acid, and chromic acid have all been recommended. In the analysis of baking-powders, no acid is required because water alone causes the decomposition; therefore the flask *F* must be perfectly dry at the start.

If the substance contains besides the carbonate a sulfide which is decomposable with acid, introduce before *A* and *B* a tube containing pumice impregnated with copper sulfate.[1] This serves to absorb all the hydrogen sulfide evolved.

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[1] Cover 60 g of pumice pieces in a porcelain dish with a concentrated solution of 30-35 g of copper sulfate. Evaporate the solution to dryness with constant stirring, and heat the residue at 150-160° for 1-5 hours.

Procedure. First make sure that the apparatus is tight. Have the flask G empty, but pour enough water in the flask F to seal the end of the tubing. Close the pinchcock I on the rubber tubing at the extreme left of the apparatus so that air cannot enter there, and make sure that all the rubber stoppers are inserted tightly in the necks of the four flasks. Open the screw clamp K a little and apply gentle suction so that at first about 2 bubbles of air per second will pass through the liquid in B. If the apparatus is tight the current of air will soon slow down. When the air is passing at the rate of about 1 bubble in 2 seconds, close K tightly and take the rubber tubing off the suction pipe. There should now be no movement of air through the liquids in F or B. After a few minutes, carefully allow air to enter the apparatus through the tubing at I by squeezing the end of the tubing to the left of I between the thumb and finger and alternately releasing the pressure at I and between the fingers. If the apparatus is tight, about as many bubbles of air will flow through the apparatus as were withdrawn during the evacuation.

During this testing, the tube D, which has been wiped dry with a clean linen cloth, should be resting in the balance case. After it has been there at least 10 minutes, remove the rubber tubing from the ends of the capillary tubing and weigh it and its contents to 0.1 mg. Weigh accurately 0.5–0.6 g of carbonate into the dry flask F, and add enough water to seal the end of the tubing at the bottom of the flask. Connect the weighed Ascarite tube to the front end of the train, place about 50 ml of approximately N hydrochloric acid in the flask G, and make sure that the pinchcock I is open. Apply gentle suction, and regulate the screw clamp K so that about 2 bubbles of gas per second pass through the sulfuric acid in B. When all the acid has been drawn from G into the flask F, start heating the contents of F. During the heating, watch the glass tubing that connects the flasks F and G and do not let the liquid pass from F toward G, as will happen if the liquid in F is heated too rapidly. If the liquid starts going toward G, turn down the flame and, if necessary, increase the suction. Finally boil the liquid in F for 1 minute. Then take away the flame and continue drawing air through the apparatus, at the rate of 2–3 bubbles per second, for 20 minutes longer, in order to get all the CO_2 into the absorption tube D. After this, detach D from the train and connect the two open ends with a piece of rubber tubing, to prevent absorption of CO_2 from the air. Wipe the tube carefully with a piece of clean linen and allow it to stand in the balance case for 15 minutes. Remove the rubber tubing and weigh. The gain in weight represents absorbed CO_2.

Remark: The results obtained by this method are perfectly satisfactory. For the analysis of substances containing small amounts of carbonate, take 3–10 g for

the analysis. It is convenient to use another Midvale tube as a tare when weighing the tube D, then recording merely the difference in weight. Sulfites interfere with this determination, but the difficulty can be overcome by decomposing the carbonate with an excess of potassium dichromate solution and adding the dilute acid later.[1]

When many analyses are to be made, it is well to use another Midvale tube in the train; as soon as this tube gains noticeably in weight because the absorption of CO_2 in the first tube is incomplete, use the second tube for the analysis and refill the first tube with Ascarite. Ascarite will absorb about 20 per cent of its weight of CO_2.

Determination of Total Carbonic Acid in Mineral Waters

Place 3–4 g of freshly burnt lime[2] and the same amount of crystallized calcium chloride[3] in each of 4 to 6 Erlenmeyer flasks. Close the flasks by means of tightly fitting rubber stoppers and weigh accurately. Take a double-bored rubber stopper of such a size that it will fit into the neck of each of the above flasks and through one of the holes fit a short glass tube which reaches about 3 cm above the stopper and the same distance below, and through the other hole insert a glass tube about 50 cm long which likewise reaches about 3 cm below the stopper. To fill the weighed flasks with the water to be analyzed, take them to the spring, and fill one after another as follows: Replace the solid rubber stopper by the one fitted with the two tubes, hold the thumb over the shorter of the tubes, and dip the flask well below the surface of the water, but so that the longer tube still reaches into the air above. Now remove the thumb from the shorter tube; the spring-water will pass into the flask and the replaced air will escape through the long tube. As soon as the flask is almost full, again close the shorter tube with the thumb, remove the flask from the water, and once more quickly interchange the stoppers.

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[1] E. R. Marle, *J. Chem. Soc.*, **95**, 1491 (1909). If it is desired to determine a small quantity of carbon dioxide in a gas containing considerable hydrochloric acid and hydrogen sulfide, use a tube containing finely divided metallic copper, instead of the pumice and copper sulfate, to absorb the hydrogen sulfide, and a tube containing *p*-nitrosodimethylaniline to absorb hydrochloric acid, Vernon and Whithy, *J. Soc. Chem. Ind.*, **47**, 257 (1928).

[2] To prepare this lime absolutely free from carbonate, place the lime in a tube of difficultly fusible glass and heat in a small combustion furnace, meanwhile passing a current of dry air free from carbon dioxide over it. In this way 4 g of commercial lime can be freed from carbonate in 30–45 minutes. That the carbon dioxide is actually removed can be shown at the end of that time by passing the escaping air through baryta water; there should be no turbidity. A blank experiment should always be made with this lime. If it is desired to use commercial lime for the determination, determine the amount of carbonate present and use an accurately weighed amount for the analysis.

[3] The addition of calcium chloride serves to decompose any alkali carbonate. This is not quantitatively decomposed by lime alone, particularly when magnesium carbonate is present.

To make sure that the solid stopper is not loosened while carrying the flask hack to the laboratory, cover it with a piece of parchment paper, and tie it with string to the neck of the flask. Allow the flasks and contents to stand several days with frequent shaking. All the carbonic acid of the spring-water will then have reacted with the lime and be precipitated as calcium carbonate. Allow the precipitate to settle, and weigh. The gain in weight represents the weight of water taken. Quickly pour off the supernatant liquid through a plaited filter, quickly throw the filter and its contents into the decomposition flask, connect with the train shown in Fig. 44, and determine the carbon dioxide as in the previous method.

This method is capable of yielding excellent results provided that the flasks can be filled as above described. Often, however, the spring is not easily accessible, so that the flasks must be filled by a different method and usually a small amount of carbonic acid is lost during the operation. A much more expeditious and accurate procedure which can be performed within 1 hour at the spring consists in the determination of the total amount of carbonic acid present in mineral waters by measuring the volume of the gas.[1]

Gas-volumetric Determination of Carbonic Acid

(a) Method of O. Pettersson[2]

This excellent method, upon which the two following procedures are based, consists in evolving carbon dioxide from carbonates by the action of acid, collecting the gas over mercury and computing its weight from its volume. Pettersson's apparatus, shown in Fig. 45, was used by him for the determination of the carbonic acid in sea-water and in carbonates, and also for the determination of carbon in iron and steel. The procedure for determining the carbonic acid in a water containing small amounts of free carbonic acid but considerable carbonate will suffice to show how the apparatus is used. Fill the decomposition flask K with distilled water up to the mark just below the side arm (the mark is not shown in the illustration). By weighing the flask both empty and with this amount of water, the volume of the flask when filled to the mark is obtained. Drop in a small piece of aluminum wire[3] and connect the flask with the rest of the apparatus as shown in the figure. All the rubber tubing should he firmly fastened to the glass by means of wire. Close the cocks, a, b, and d, open c, and remove the air in the measuring

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[1] Cf. the modified method of Pettersson on p. 336.

[2] *Ber.*, 23, 1402 (1890).

[3] At 720 mm and 15° C, 0.0142 g aluminum evolves 20 ml of moist hydrogen.

tube by raising M until the mercury rises in the capillary up to the crossing point. After this close c, open a, lower M, and slowly open the screwcock d. By this means the hydrochloric acid in N is introduced into the flask K. Allow the acid to run into the flask until the upper part of the apparatus is reached, then close d and a. Remove the air in the measuring tube (which does not contain an appreciable amount of carbon dioxide) by opening c and raising M, after which again close c. Now once more open a, lower M, and heat the liquid in K by a flame.

A lively evolution of gas at once ensues. As soon as the measuring tube is almost filled with the gas, close a, draw the flame from under K, raise M until the mercury within it stands level with that in the measuring tube, and read its position in the latter. At the same time note the barometer reading and the temperature of the cold water which surrounds the measuring tube. After this open b and raise M, whereby the gas passes into the Orsat tube O which contains caustic potash solution (1:2). As
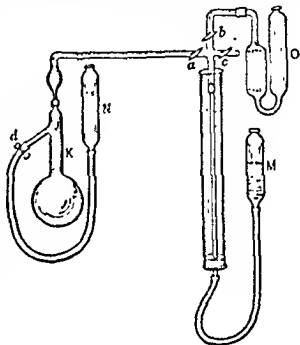
Fig. 45.

soon as the mercury has reached the juncture of the horizontal and vertical tubes, close b and allow the gas to remain in the Orsat tube for 3 minutes. Once more transfer the unabsorbed gas into the measuring tube, taking care that none of the caustic potash solution comes with it (the latter should not quite reach the stopcock b). After bringing the gas to the atmospheric pressure, read the volume of the gas, the thermometer, and the barometer. As a rule, these readings of the barometer and the thermometer remain constant; otherwise it is necessary to reduce the gas volumes in each case to 0° C and 760 mm pressure. The difference between the two volumes represents the amount of the carbonic acid gas. Remove the unabsorbed gas through c and a, repeat this whole operation of collecting the gas and absorbing the carbon dioxide until finally no more gas is given off from the liquid in K.

If it is desired to determine the amount of carbonate in a solid substance, a smaller decomposition flask should be used. Add the aluminum wire to the weighed substance and exhaust the apparatus by re-

peatedly lowering M, closing a, opening c, and then raising M. Finally allow the acid to act upon the substance and carry out the determination exactly as described above.

Computation of the Analysis. Assume that from a g of substance V ml of carbon dioxide was obtained, which was measured moist at $t°$ C and B mm pressure. First of all reduce the volume to 0° C and 760 mm pressure by the following formula:

$$V_0 = \frac{V(B-w)\cdot 273}{760(273+t)}$$

In this formula, w represents the tension of aqueous vapor expressed in millimeters of mercury.

Since the gram-molecular volume of carbon dioxide is 22.26 l, 1 ml CO_2 weighs 44.01/22,260 = 0.001977 g at 0° and 760 mm, and V_0 ml weighs $V_0 \times 0.001977$ g. The percentage of CO_2 in the original substance is then

$$\frac{V_0 \times 0.1977}{a} = \text{per cent } CO_2$$

Remark. The addition of aluminum is absolutely necessary. By boiling an acid solution, carbonic acid is not completely expelled; this is effected only when a different gas simultaneously passes through the solution. Formerly it was customary to pass air through the apparatus, but Pettersson accomplished the same purpose by generating hydrogen within the liquid itself.

(b) *Method of Lunge and Marchlewski*[1]

Lunge and Marchlewski carry out the determination according to the same principle as that of the above procedure, i.e., by simultaneously evolving hydrogen (aluminum and hydrochloric acid), measuring the gas, and absorbing the carbon dioxide by means of caustic potash in an Orsat tube.

The apparatus which they recommend is shown in Fig. 46, b. It consists of the 40-ml decomposition flask N, the 140-ml measuring tube A, the compensation tube C, and the leveling tube B; the three last are connected together as shown in the figure.

In all gas-volumetric methods, the volume of the measured gas must be reduced to 0° C and 760 mm pressure, which ordinarily requires a knowledge of the temperature and the barometric pressure. In this method the reduction is accomplished without paying any attention to the actual readings of the thermometer and barometer by means of the compensation tube C, which contains a known amount of air, viz., that

amount of air which in a dry condition assumes a volume of 100 ml at
0° C and 760 mm pressure. If, therefore, this amount of air has a volume
of V' at $t°$ and atmospheric pressure P' (with the mercury at the same
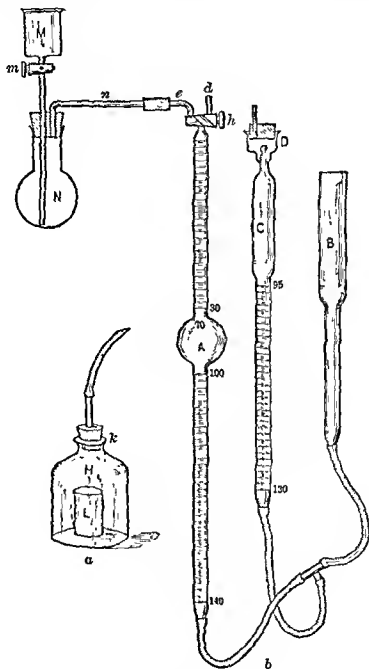
Fig. 46.

level in B and C), we know that this volume of any gas would be equal
to 100 ml at 0° C and 760 mm pressure. By raising the leveling tube B
so high that V' ml is compressed to 100 ml, we have accomplished the

reduction in a mechanical way. If, however, there is a gas volume V'' in the measuring tube A under the same pressure as that in the compensation tube (this is the case when the mercury level is the same in A and C), we can reduce this volume to the standard conditions by simply raising B until the volume of the gas in C is just 100 ml, taking care that the mercury remains at the same height in the tubes A and C. The volume of the gas V_0'' in A corresponds, therefore, to the volume of this gas at 0° C and 760 mm pressure, for it has been compressed to the same degree as the gas in C. This is apparent when we remember that at a constant temperature the product of the pressure into the volume remains a constant for any gas.

In the compensation tube we have the volume V' at atmospheric pressure P', and after compression the volume becomes $V_0' = 100$ ml and the pressure is P_0, from which it follows that:

$$(1) \qquad V'P' = V_0'P_0$$

In the measuring tube A, we have the volume V'' at the atmospheric pressure P', and after compression this volume becomes V_0'', and the pressure P_0, so that

$$(2) \qquad V''\cdot P' = V_0''P_0$$

By dividing equation 1 by equation 2 we have:

$$\frac{V'\cdot P'}{V''\cdot P'} = \frac{V_0'\cdot P_0}{V_0''\cdot P_0}$$

or

$$V':V'' = V_0':V_0''$$

and V_0'' is, therefore, the reduced gas volume that is desired.

Before using the apparatus for the determination, it is necessary to fill the compensation tube with the correct amount of air; this is accomplished as follows:

First of all, calculate what would be the volume of 100 ml of dry air measured at 0° C and 760 mm pressure when measured moist at the temperature of the laboratory and the prevailing barometric pressure. To illustrate, assume $t = 17.5°$ C; $B = 731$ mm; $w = 14.9$ (tension of aqueous vapor); then

$$V = \frac{100 \times 760 \times 290.5}{273(731 - 14.9)} = 112.9 \text{ ml}$$

In such a case introduce 112.9 ml of air into the tube C by removing the stopper and lowering the leveling tube until the mercury in the compensation tube stands at exactly 112.9 ml. Add a drop of water by a pipet, immediately stopper the tube, and make an airtight seal by covering the tube with mercury. Then press down a rubber stopper containing a glass tube into D. After this the temperature and pressure may vary as much as it will; the reduced volume of the air in C will always be equal to 100 ml.

Procedure for the Analysis. Weigh out about 0.08 g of aluminum wire, i.e., enough to furnish approximately 100 ml of hydrogen, into the decomposition flask. Add a sufficient weight of the substance to be analyzed so that about 30 ml and no more of carbon dioxide will be generated, and connect the flask with the funnel tube M, and capillary n. Also make connection with the tube A after it has been completely filled with mercury by raising B. Exhaust the air from N by lowering B, opening h so that e is connected with A, then closing h by turning it 90°, and carefully raising B until the mercury stands at an equal height in A and B; after this turn h so that A is connected with the capillary d, and expel the air in A. After repeating this process 3 or 4 times until finally only 2–3 cm of air remains in A, lower B, add the necessary volume of 3 N hydrochloric acid to M, carefully open h, then m until 10 ml of the acid has run into the flask N, when m is once more closed. The carbon dioxide evolution begins at once and the mercury level in A quickly falls in A. Heat the contents of the flask to boiling over a flame and maintain this temperature until all the aluminum has dissolved. During the whole operation the mercury level in B must be kept lower than that [in A. In order to transfer the gas remaining in the flask N into the tube A, fill M with distilled water, slowly open m, and allow the water to run into N until the stopcock h is reached, then immediately close h. Compress the gas by raising the tube B until the mercury stands at the same height in A and C and the level in the latter tube is exactly at the 100-ml mark. Read the volume of the gas. After this connect the capillary d with an

Fig. 47.

Orsat tube filled with 10 N caustic potash (Fig. 47), drive over the gas in A into the Orsat tube, allow to stand 3 minutes, and transfer the unabsorbed gas to A, where its volume at 0° C and 760 mm pressure is determined as before. The difference in the two readings represents the volume of the carbon dioxide, and the percentage can be computed according

to the formula

$$\text{Per cent } CO_2 = 0.1977 \cdot \frac{V}{a}$$

in which V is the weight of carbon dioxide absorbed in the Orsat tube and a represents the quantity of substance taken for the analysis.

Remark. This is the most exact of all methods for the determination of carbon dioxide in solid substances and is accomplished quickly. It is to be recommended where carbon dioxide determinations must be made daily, as, for example, in cement factories. It is necessary, however, to test the volume of the gas in the compensation tube from time to time to make sure that it really corresponds to 100 ml of air under the standard conditions of temperature and pressure.

For a single determination the author prefers to dispense with the compensation tube. In this case, however, the collected gas must be kept surrounded by water at a definite temperature, as in the Pettersson method, and the temperature and pressure must be observed. It is also well to make these readings in the above-described procedure, to be sure that the volume in the compensation tube has remained constant.

(c) Method of Lunge and Rittener[1]

In the decomposition flask K, Fig. 48, place 0.14–0.15 g of calcite, or a corresponding amount of any other carbonate, and fasten a small piece

FIG. 48.

of aluminum wire, weighing about 0.015 g, to the neck of the flask. Allow about 1 ml of water to flow through the funnel, T, and then connect the capillary with the dry Bunte buret. Close the stopcock of the funnel T and open the two cocks of the Bunte buret. Connect the lower stopcock, h_1, with the suction pump, and produce a partial vacuum in the buret by letting the pump run 2–3 minutes, after which close h_1. Now, from the funnel T, allow 2.5 N hydrochloric acid to flow upon the substance until it is decomposed completely; then heat the liquid to boiling,[2] taking care that no water gets into the buret. Add acid from T until the aluminum wire is reached and heat the flask again. The hydrogen now evolved serves

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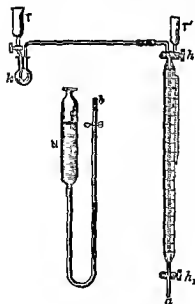
[1] *Z. angew. Chem.*, 1906, 1849.

[2] Carbonates, such as magnesite, dolomite, or siderite, are decomposed so slowly by cold, dilute acid that it may be added much more quickly than prescribed above.

to expel the last traces of carbon dioxide from the flask. As soon as all the aluminum is dissolved, add hydrochloric acid through the funnel until the liquid reaches the stopcock h, which is then closed at once. Now connect the lower end, a, of the buret by rubber tubing with the leveling tube N, which contains a saturated solution of common salt. By carefully opening the lower stopcock h_1 allow the salt solution to rise in the buret until the liquid there stands at the same height as in the leveling tube, whereupon the stopcock h_1 is closed. Allow the apparatus to stand for 20–25 minutes so that the temperature of the gas will be that of the surroundings and then, by suitably raising or lowering the leveling tube with h_1 open, read the buret, the thermometer, and the barometer. Fill the funnel T' of the buret with strong potassium hydroxide solution (1:2), and produce a partial vacuum in the buret by lowering the leveling tube and opening the stopcock h_1.

Allow the caustic potash solution to run into the buret by opening the upper stopcock h, but close it before the last few drops of liquid leave the funnel. Mix the contents of the buret by shaking. By repeating the operation it is easy to tell whether the absorption of carbon dioxide has been complete. Read the residual volume with the usual precautions; the difference between the two readings gives the volume of the carbon dioxide.[1]

Compute the weight of carbon dioxide exactly as described on p. 330, except that the vapor tension of the saturated salt solution amounts to only 80 per cent of the tension of pure water at the same temperature.

Example: Weight of substance = a Temperature = $t°$
Volume of hydrogen + air + CO_2 = V_1 Barometer = B mm
Hydrogen + air = V_2 Tension of aqueous vapor = w mm
$CO_2 = V_1 - V_2$ Tension of salt solution = $0.8w$ mm

The volume reduced to 0° and 760 mm, is, therefore:

$$V_0 = \frac{(V_1 - V_2) \cdot (B - 0.8w)\ 273}{760\ (273 + t)}$$

and the percentage of CO_2 in the substance (see p. 330) is

$$\frac{V_0 \times 0.1977}{a} = \text{per cent } CO_2$$

For the determination of carbon dioxide in mineral waters this apparatus is not suited, for this purpose Treadwell modified the Pettersson apparatus as shown in Fig 49.

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[1] This is true if the temperature and pressure are the same as before the absorption of the CO_2. If not, both volumes must be reduced to 0° and 760 mm pressure before the difference is found.

(d) The Modified Method of Pettersson

For decomposition flasks, use 70–200 ml Erlenmeyers (according to the supposed amount of carbonic acid) and etch the exact capacity of each flask upon it. To determine this, provide each flask with a tightly fitting stopper of gray (not red) rubber containing one hole, through which the small tube R is introduced. Fuse together the bottom of R but near the bottom make a small hole.
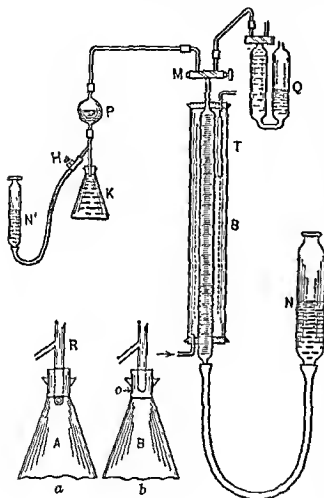
Fig. 49.

Push the tube R into the stopper until the small opening can be seen just below the bottom of the rubber stopper, and press the stopper as far as possible into the Erlenmeyer flask full of water. By this means some of the water passes from the flask into the tube R. Then raise the latter as is shown in Fig. 49, b; in this way an air-tight seal is made.

Remove the water in R by filter paper, and weigh the flask and contents to the nearest centigram. By deducting from this the weight of the empty flask together with the rubber stopper and R, the weight of the water, i.e., the volume of the flask, is obtained. By means of a piece of gummed paper fastened to the flask, note the position of the lower edge of the rubber stopper. Empty the flask, dry, and cover the neck of the flask as well as the paper strip with a thin coating of paraffin wax. Along the edge of the paper where the bottom of the rubber stopper came on the flask, cut a sharp line in the wax by means of a knife and write the capacity upon the wax with a pointed file. Etch these lines upon the flask by exposing them to the action of hydrofluoric acid for 2 minutes. Wash off the excess of the acid, dry the flask, melt the wax, and wipe off with filter paper. The flask is now ready to be used for the analysis.

Place about 0.04 g of aluminum in the flask, and fill it by dipping into the spring. When this is not possible, place a piece of rubber tubing in the bottle containing the water to be analyzed, so that it reaches to the bottom, and siphon the water into the flask for 2-3 minutes. After this, close the filled flask by the rubber stopper with the tube R so that the bottom of the stopper reaches just to the mark again. Raise the tube R (Fig. 49, a) and wash out the spring-water within the tube by a stream of distilled water from a wash bottle.[1] Then connect the flask with the bulb tube P (of about 40-ml capacity), which in turn is connected with the measuring tube B. Place B in a condenser through which a stream of ordinary water constantly flows. Now connect the reservoir N' with the flask as shown in the figure and close the screwcock H. All rubber connections must be tightly fastened with wire.

Exhaust the bulb P by lowering N so that the air passes into B, whence it is driven into the Orsat tube O by turning the stopcock M and raising N. Repeat this operation 4 times. Then remove the air from the Orsat tube by suction through the right-hand capillary and change the stopcock to its original position as shown in the figure. Now press down the tube R into the flask so that the small opening reaches below the lower surface of the stopper.

Usually carbon dioxide is evolved immediately and at once the mercury in B begins to sink slowly. Hasten the evolution of the gas by gently heating the contents of the flask. As soon as the measuring tube is almost entirely filled with gas, remove the flame, close M, and bring the contents of B under atmospheric pressure by raising N until the mercury in the two tubes is at the same height, and read its position in B. Take the temperature of the water surrounding B, read the barometer,[2] drive the gas over into the Orsat tube, and allow it to remain there. Repeat this boiling, measuring, and driving over of the gas until only a slight evolution of gas can be made to take place. In this way all the free carbon dioxide and a part of that present as bicarbonate is driven off, while that present as normal carbonate together with the rest of the bicarbonate remains in the flask; the liquid in the flask is usually turbid at this point owing to the precipitation of alkaline-earth carbonates. Now fill the reservoir N' with 4 N hydrochloric acid (1 : 2) and remove the air from the rubber tubing by raising N' high and pinching the tubing with the fingers. Place the leveling tube N in a low position, open H, and allow a little acid to run into K, after which H

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[1] With water containing much carbonic acid, cool the flask and its contents by ice in order to prevent it from breaking
[2] If this analysis is made at the spring, it is necessary to have a sensitive aneroid barometer at hand

is again closed. As soon as the acid reaches the contents of K, a lively evolution of carbon dioxide ensues, which is afterward hastened by gentle warming. When the measuring tube B is nearly filled, read its contents and drive over into the Orsat tube as before. Repeat the addition of the acid, etc., until finally the liquid in K clears up and the aluminum begins to evolve a steady stream of hydrogen, then heat the contents of the flask to boiling, but take care that none of the liquid in the flask is carried over with the escaping gas. As soon as the aluminum has completely dissolved, lower N and open H so that the flask is filled with the hydrochloric acid solution and the last portions of the gas are carried over into the measuring tube B. As soon as the acid has reached the stopcock M, close it, and after reading the volume of the gas as before, transfer it to the Orsat tube. After it has remained there 3 minutes bring back the unabsorbed gas to B and subtract its volume from the total amount of gas which has been expelled from the water that was analyzed. This difference represents the volume of the carbon dioxide gas. By correctly adjusting the current of water flowing through the condenser, the temperature at which the gas is measured will remain constant during the entire experiment.

From the volume of the absorbed carbon dioxide the percentage present is computed as was shown under the Pettersson method.

Determination of Carbonic Acid in the Air

See Chapter XV, "Acidimetry."

Determination of Carbonic Acid in the Presence of Other Volatile Substances

(a) Determination of Carbonic Acid in the Presence of Chlorine

If it is desired to determine the amount of carbonate present in commercial chloride of lime, chlorine will be evolved with the carbonic acid on treatment of the solid substance with hydrochloric acid, so that neither the direct nor the indirect method will give correct results. The determination can easily be effected by the following procedure:

Decompose the chloride of lime with hydrochloric acid and pass the evolved gases $(CO_2 + Cl_2)$ into an ammoniacal solution containing calcium chloride.[1] After allowing to stand several hours in a warm place, quickly filter off the precipitate, wash with water, and determine

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[1] Dissolve 50 g of crystallized calcium chloride in 250 ml of water, add 500 ml of concentrated ammonia water, and allow the mixture to stand at least 4 weeks before using.

the carbonate in the precipitated calcium carbonate by one of the usual methods.

Remark. On conducting the mixture of chlorine and carbon dioxide into the ammoniacal solution of calcium chloride, the chlorine is changed into ammonium chloride with evolution of nitrogen, $8NH_3 + 3Cl_2 = 6NH_4Cl + N_2$, while the carbon dioxide is absorbed by the ammonia, forming ammonium carbonate, which is precipitated by the calcium chloride as calcium carbonate.

(b) Determination of Carbon Dioxide in the Presence of Alkali Sulfides, Sulfites, or Thiosulfates

Treat the solution to be analyzed with an excess of a solution of hydrogen peroxide containing potassium hydroxide, but free from carbonate. Boil to destroy the excess of the hydrogen peroxide, concentrate, and determine the carbonate preferably by the Fresenius-Classen method (p. 325).

DETERMINATION OF CARBON

(1) *In Iron and Steel.*
(2) *In Organic Compounds.*

Carbon occurs in iron and steel as carbide, as a solid solution of carbide in iron, as graphite, and as temper carbon. Iron carbide, Fe_3C, is often called cementite. The properties of iron and steel depend not only upon the chemical composition of the material but also upon the treatment which has been given to it. Thus a steel with a given percentage of carbon may be very hard if it has been cooled quickly from say 1000°, or it may be much softer if it has been annealed. By polishing a piece of metal and etching the surface, it is possible to estimate by microscopical examination the percentage of carbon present, the heat treatment which has been given to the specimen, and whether the material is homogeneous. In testing steel and other alloys the work of the chemist should go hand in hand with that of the metallographer as either is likely to be led astray without the other.

Here we shall assume that steel is a binary alloy of carbon and iron. This will carry us sufficiently into the field of metallography but it must be remembered that other elements, e.g., manganese, sulfur, silicon, chromium, nickel, tungsten, and vanadium, play important parts in modern steel-making. To understand the reasons for the various effects accomplished by heat treatment, it is necessary to know something concerning the laws of physical chemistry, especially the phase rule of Willard Gibbs. Here just a little of the theory will be touched upon.

The mass-action law, which has frequently been mentioned in this book, refers to what is called *homogeneous equilibria*. It governs, for example, the reaction between ions when everything is present in a state of aqueous solution. We say that this constitutes a single *phase*. Every homogeneous state which the components of a system can produce is called a *phase*; the phases, in other words, are the physical states in which the components can exist. A few illustrations will help here.

The compound H_2O can exist as solid, liquid, or gas, and each of these physical states represents a phase. A mixture of NaCl and H_2O can exist in four phases. If, at a low temperature, the two compounds exist side by side as solids which are distinguishable from one another (ice and salt), we say that two phases are present and the system is not homogeneous. As many solid phases can exist side by side as there are distinguishable solids. If we have a solution of NaCl in water, we have a single phase, and we say that we have a homogeneous system. If we add more water, more salt, or any other substance to the solution (and there is no precipitation), we still have but a single phase. If, on the other hand, we add ether to an aqueous solution, and can distinguish a line of demarcation between the two liquids, we have two phases. In any system there can be as many liquid phases as there are immiscible liquids or solutions. Gases, however, all mix with one another and constitute a single phase. What Gibbs did was to discover an important relation between the number of components, the number of phases, and the degrees of freedom of a system.

If we study the equilibrium conditions of water with respect to its existence as solid, liquid, or gas, we say that we are considering a *one-component* system. The number of components is the smallest number of independently variable constituents required to build up the system. In studying the reaction $CaCO_3 \rightleftarrows CaO + CO_2$ we say that we have a *two-component* system because any desired state can be obtained from suitable quantities of CaO and CO_2 and it is not necessary to have all three present at the start. On the other hand, it is not a one-component system because it is not possible to get all sorts of mixtures of CaO and CO_2 from $CaCO_3$ alone.

In studying the equilibrium of a gas we determine pressure and temperature. If both temperature and pressure can be varied without changing the number of phases present, we have two *degrees of freedom*. In studying a solution of a definite substance in water we measure temperature and concentration, and we say that there exist two degrees of freedom if we can vary the temperature and concentration without causing the number of phases to change.

The Gibbs rule is

$$P + F = C + 2$$

when P is the number of phases, C is the number of components, and F the degrees of freedom in a state of equilibrium.

This is a very important generalization. Let us take a few examples. If we study the equilibrium conditions of a one-component system such as water, we find that we can express all possible conditions in terms of the two variants pressure and temperature. At 0.0076° and 4.57 mm of aqueous pressure, we can have existing together in perfect equilibrium the three phases, ice, water, and water vapor. Then applying the phase rule we have

$$3 \text{ phases} + 0 \text{ freedom} = 1 + 2$$

There is no freedom to the system when ice, water, and water vapor are existing together in a state of perfect equilibrium, and we have a state of *invariant* equilibrium. On the equilibrium diagram there is such a so-called *triple point* at 0.0076° and 4.57 mm pressure.

The system salt and water can be expressed in terms of concentration of the solution and temperature. At −22° and with about 23 per cent of dissolved sodium chloride, there can exist four phases in equilibrium side by side, and we have what is called a *quadruple* point. The four phases are water vapor, liquid solution, solid ice, and solid salt. If either the concentration of the solution or the temperature is changed, one phase will disappear. For a two-component system, $P + F = 2 + 2$; and when all four phases are present together, there is no freedom and the system is in a state of invariant equilibrium.

The alloys of iron and carbon can be studied on this basis. In reality the alloys contain more than two components, Fe and C, but it is simplest to study them on this basis and then find the effect that other constituents exert. Figure 50 is an
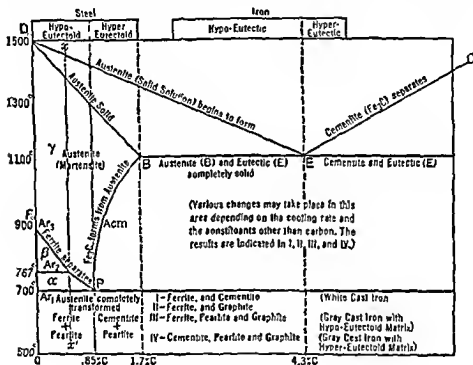
Fig. 50.

equilibrium diagram of iron and carbon. Temperatures are plotted as ordinates and concentrations of carbon as abscissas.

In applying the phase rule to this diagram, it is assumed that the vapor phase is always present although to an inappreciable extent. Neglecting this phase, the rule becomes $P + F = C + 1$, which means that the system has no freedom, or is *invariant*, when three solids or two solids and a liquid exist together. If the temperature is changed, one phase disappears. The diagram shows two such points, E and P. At E (1.3 per cent C and 1100°) the melt can exist in equilibrium with two solids, called *austenite* and *cementite*. The intimate mixture of these two phases which exists in equilibrium with the molten metal at E is called *eutectic*. Cementite is the metallographic name given to Fe_3C; austenite is the name given to a solid solution (mixed crystals) of Fe_3C in Fe. According to its appearance under the microscope, the solid solution of Fe_3C in Fe is given different names. Austenite may be assumed to repre-

sent the solid solution in the state in which it exists nt high temperatures. On cooling it tends to break down into iron and cementite, and the point P on the diagram is where an intimate mixture of Fe and Fe$_3$C, called *pearlite*, is in equilibrium with the solid solution of Fe$_3$C in Fe. As the austenite breaks down into Fe and Fe$_3$C, it passes through the stages called martensite, troostite, and sorbite. The transition to martensite takes place so readily that austenite is seldom found in commercial steels. Troostite and sorbite have been called colloidal solutions of Fe$_3$C in Fe.

The point P on the diagram has been called the *eutectoid* point, but the name pearlite is commonly given to the Fe-C alloy of this composition because, when the annealed sample is polished and etched slightly, the " eutectoid " shows under the microscope a luster similar to that of mother-of-pearl.

If a sample of Fe-C alloy with, say, 1 per cent of carbon is cooled slowly from the molten state and the temperature is plotted against the time, the rate of cooling will lag a little, showing an evolution of heat due to the separation of a solid, when the line DE is reached. The solid that separates out is austenite of the composition corresponding to that temperature, as is shown by drawing a horizontal line across to the line DB. As the temperature falls, the freezing point of the alloy follows the line DE and the carbon content of the solid solution follows the line DB. Since less than 1.7 per cent carbon is present, the only product on solidification will be austenite. If more than 1.7 per cent of carbon is present some eutectic will be formed at 1100°, the amount increasing as the C content approaches 4.3 per cent; an alloy of 4.3 per cent C and 95.6 per cent Fe will solidify entirely at 1100° and show a melting point as sharp as if it were a pure compound.

The region above the lines DEC in the diagram represents molten metal and a field of bivariant equilibrium. The region $DBPF$ represents austenite, or solid solution, and another field of bivariant equilibrium. The lines FPB show where the solid solution should break down, and on these lines there is univariant equilibrium except at the point P. FP shows where pure Fe separates out until, at 700°, pearlite is deposited. The line BP is where Fe$_3$C separates out.

On the diagram three critical points are shown at Ar_1, Ar_2, and Ar_3. These are said to mark three allotropic forms of Fe: α-Fe is stable below 767°, β-Fe between 767° and 900°, and γ-Fe above 900°. Carbon is soluble only in γ-Fe, so that I may say that the field $DBPF$ represents the region where a solution of C (or of Fe$_3$C) in γ-Fe exists.

All the transformation points in the equilibrium diagram are found a few degrees higher when they are approached with rising temperature, and that is why a distinction is made between Ar_1, Ar_2, Ar_3 and Ac_1, Ac_2, Ac_3, the letters r and c referring respectively to the French words *refroidissement* and *chauffage*.

A sample of steel cooled slowly so that all the transformations are allowed to take place should contain ferrite + pearlite if it contains less than 0.85 per cent C and cementite + pearlite if it contains more than 0.85 per cent C. If the steel is cooled rapidly (quenched) from a temperature above the FPB line, the condition existing at the temperature from which the quenching took place is retained. The steel is in a strained state and is very much harder than if it had been allowed to cool slowly. If the steel is heated the transformation into the stable condition begins to take place before the FPB line is reached

On slow cooling of *irons* the metal should consist of austenite + eutectic or cementite + eutectic, but the Fe$_3$C is not very stable and it may break down into Fe and C. The presence of silicon tends to hasten this change, and when the C has deposited as graphite we have a *gray cast iron*. Sulfur tends to prevent this breaking

down of the Fe_3C, and when no graphite is formed we have a *white cast iron* which is very hard and also brittle.

This is not the place to go deeply into the metallography of iron and steel, but it seems desirable that every analyst should know that the condition of the carbon is just as important as the quantity of carbon in determining the properties of steel and that the heat treatment given the steel may change its properties entirely.

The chemist distinguishes between total carbon, combined carbon, and graphite. In steel, usually no uncombined carbon is present; and although attempts have been made to distinguish between combined carbon that is present as cementite, Fe_3C, and that present in solid solution (martensite, austenite, etc.), which has been called "hardening carbon," the total carbon is the only determination that the chemist is usually asked to make on steel. In the analysis of irons, usually the total carbon and the graphite are determined and the combined carbon is found by difference.

In the chemical analysis of iron and steel the total carbon is usually obtained by combustion. In this country, this is usually done in the dry way with an electric furnace. In some parts of Europe a wet combustion, or oxidation by a mixture of chromic and sulfuric acids, is preferred. For a long time it was considered desirable to remove the iron by volatilization in a stream of chlorine (Wöbler) or by treating the metal with a solution of double chloride of copper and potassium (Berzelius-Richter), but at a temperature of 1100° it is possible to get complete oxidation of the sample without removing the iron, and the procedure is thus shortened.

The combined carbon is sometimes determined quickly by matching the color of the solution obtained by dissolving the steel in nitric acid, but the color is not strictly proportional to the carbon content and a hardened steel gives a different color from that given by an annealed steel with the same carbon content. If speed is required, it is possible to determine carbon by combustion in less than 10 minutes, so that there is no longer any excuse for carrying out the colorimetric determination except in small steel works with limited laboratory equipment.

The carbon content can be estimated quite closely by means of a microscopic examination of the etched, polished surface of a sample of steel. Spark testing has also been used. In the old days the steel was "struck" with flint but later ~ ~ grinding wheels were made it possible to c

electrical-resistance or Enlund method is based upon the fact that elements dissolved in iron increase the specific electrical resistance by an amount inversely proportional to their atomic weights, and carbon can be held in solid solution or thrown out at will in the case of steels by cooling slowly or by quenching. The difference between the specific electrical resistance of a properly prepared and quenched sample and that of the same or a similar specimen which has been annealed or normalized gives a factor from which the percentage of carbon can be calculated. Finally the magnetic method depends upon the fact that the incremental permeability of steel as measured by the deflection of a ballistic galvanometer is proportional

to the carbon content. Other alloying elements have a similar effect, so that this method of testing, which can be carried out with an instrument called the *carbometer*, is restricted to the preliminary testing of plain-carbon steels made by the open-hearth or by the Bessemer process.

In classifying steels according to the carbon content, it is quite common to call each 0.01 per cent of carbon a *point*. Thus a 10-point carbon steel is one containing 0.10 per cent carbon.

Determination of Total Carbon by Direct Combustion in Oxygen

Apparatus. A suitable arrangement is shown in Fig. 51 together with some parts that can usually be omitted. The entire set-up is called a *combustion train*, and the *front end* is on the right where the excess oxygen leaves the apparatus. Sometimes this is called the *exit end*. Beginning at the back end, *A* represents a cylinder of oxygen which can be purchased filled with oxygen of about 95 per cent purity and free from CO, CO_2, or any other acidic gas or carbon-bearing material. If oxygen
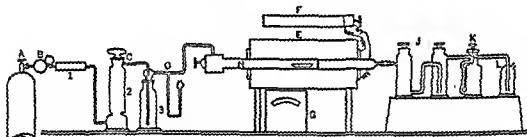
Fig. 51. Diagram of combustion train for the determination of carbon in steel.[1]

of this purity cannot be obtained, special provision must be made for purifying it in the train. *B* represents a reducing valve whereby oxygen can be forced at an easily regulated speed through the apparatus. The reducing valve must be capable of stepping down the pressure of the gas so that it can be made to leave the valve at a pressure of not more than 2 pounds per square inch and permit a steady flow throughout the train.

C represents a purifying train. With oxygen of the above-mentioned purity there is no need of this, but it is customary to insert here a CO_2 absorber, such as a soda-lime or an Ascarite tube. If the oxygen is not pure it must be passed through a tube loosely packed with ironized asbestos which is heated to about 600°. This causes combustion of CO or any other carbon compound in the gas, and the CO_2 formed is absorbed in a tube containing soda-lime or Ascarite. To prepare the ironized asbestos, saturate some well-shredded asbestos with 10 per cent ferrous sulfate solution, which is slightly acid with sulfuric acid, dry, and finally ignite at 1000° for 6 to 8 hours.

In Fig. 51, 1 represents the preheater, 2 is an absorption tube containing soda-lime or Ascarite, and 3 is a drying tube containing an efficient dehydrating agent such as fused calcium chloride, Drierite, Anhydrone, phosphorus pentoxide, or Dehydrite. It is best to use here the same absorbents for CO_2 and H_2O that are used at the other end of the train. It is important to have these gases removed with the same efficiency at both places.

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[1] *Sampling and Analysis of Carbon and Alloy Steels*, Methods of the Chemists of United States Steel Corporation.

D represents a mercury trap or manometer. It serves to give a rough idea of the prevailing gas pressure and to prevent the backflow of gas. It is not at all necessary to have this manometer, but it is convenient to have some means of knowing that the pressure of oxygen is being maintained. This is sometimes shown by inserting a liquid absorbent for CO_2 or a tube containing concentrated sulfuric acid at the front end of the apparatus, but the use of liquids is not to be encouraged except at the extreme front end of the train (L in Fig. 51).

The electric furnace is shown at E. A furnace capable of giving temperatures between 1000° and 1100° is satisfactory. It has been claimed that temperatures above 1150° are likely to cause reduction of some CO_2 before it can be taken away from around the boat, but experiments with temperatures as high as 1400° with a combustion tube at least 1.125 in. in diameter and a sufficiently rapid stream of oxygen have failed to substantiate this claim. The furnace should operate on either 110 or 220 volts A new furnace should be heated slowly to the desired temperature or the refractory may crack and crumble away from the outer insulation. Low-temperature furnaces for operating below 1100° are generally wire wound and are best operated at low voltages with an alternating current and transformer.

It is possible to make the furnace in the laboratory. To do this wrap the porcelain combustion tube in a thin sheet of asbestos and wind around it about 110 turns (40 ft) of No. 20 B and S gauge nichrome wire in a space of about 7.5 in. along the tube. Then cover the wire thoroughly with *Alundum cement*, dry, and encase it in an insulating shell. This shell should be about 6 in. in diameter and 9 in. long, packed with asbestos pipe lagging. Close the ends with disks of Transite that carry the wire terminals Laboratories where many combustions are made sometimes require multiple furnaces carrying as many as five combustion tubes.

At F in Fig. 51 is a rheostat whereby the temperature can be kept within the operating limits. With proper attachments it is possible to make the temperature control automatic, and this is advisable when many combustions are to be made.

To operate a furnace without automatic temperature control a pyrometer is necessary as temperatures above 950° cannot be judged closely with the eye. The hot junction of the thermocouple should be located within the heating chamber as near the combustion tube as possible. With temperatures above 1000° the pyrometer is not necessary except for checking the eye readings. An optical pyrometer focused on the end of the boat can be used. Gold melts at 1063°, and a correct operating temperature is one at which gold melts.

The combustion takes place preferably in a combustion tube of unglazed vitrified clay or porcelain though some brands of fused quartz can be used up to 1200°. The combustion tube should be about 28 in. long and have an internal diameter of about 1.2 in. The exit end of the tube is preferably reduced in diameter to permit connection with rubber tubing. Such a tube is shown at H in Fig. 51. The front end of the tube remains cooler if the reduction in size is made in two steps. The inlet end of the combustion tube is preferably provided with a breech connector which can be attached to the combustion tube by *plaster of paris* mixed with 2 per cent acetic acid Sometimes a ground-glass stopper fits this end of the tube. If a rubber stopper is used, it should be provided with a suitable shield against the heat or it should be water-cooled Figure 52[1] shows a breech connector which is made of brass, has a blue-glass window, and connects to the body by a bayonet joint which tightens as it is turned clockwise.

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[1] From H. Lundell, Hoffman, and Bright, *Chemical Analysis of Iron and Steel.*

GROUP III OF ANIONS

If provision is made for the absorption of oxides of sulfur in front of the combustion tube, no packing is necessary. When combustions take place continuously at 1000–1050°, the exit end of the tube can be packed with ironized asbestos to remove oxides of sulfur and selenium. After about 150 combustions, the tube should be drawn into the furnace and heated to expel the oxides of sulfur.
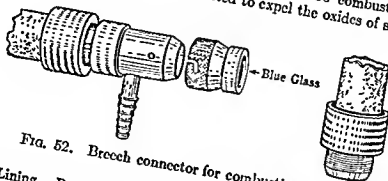
FIG. 52. Breech connector for combustion tubes.

Boats and Lining. Boats made of porcelain, refractory clays, sheet nickel, or Alundum are satisfactory. The lining or bedding material for the sample is alkali-free Alundum of 60–90 mesh, high-grade chrome ore, or Zirkite. The chrome ore should be crushed, sized, washed with dilute HCl, dried, and ignited. Zirkite is the trade name for a preparation containing natural zirconium minerals. The boat and its lining should give a blank of not over 0.0005 g when heated to 1500° in oxygen as in a combustion. To prevent injury to the combustion tube from spattering it is well to use a cover for the boat which has an opening at both ends, rests entirely upon the lining, and is high enough to permit an unrestricted supply of oxygen to reach the sample. The boat is shown at I in Fig. 51. The approximate outside dimensions are: width, 0.75 in.; depth, 0.5 in.; and length, 4–6 in.; with walls as thin as practical.

In Fig. 51, J represents a purifying train for the removal of dust, SO_2, etc. Various combinations have been recommended, such as: (1) glass wool, lead dioxide, or zinc shot and Dehydrite; (2) precipitated neutral manganese dioxide followed by Dehydrite, Anhydrone, or phosphorus pentoxide; (3) a 50 per cent solution of chromium trioxide or a 5 per cent solution of potassium permanganate followed by concentrated sulfuric acid and Anhydrone; (4) a tube containing chromium trioxide in granular form followed by a saturated solution of chromium trioxide in concentrated sulfuric acid and a tube of P_2O_5 or the same desiccant used in the preceding tube. Objections have been raised against lead dioxide, zinc shot, or any liquid in the train, and the chemists of the United States Steel Corporation prefer neutral manganese dioxide which is prepared as follows:

Dissolve 50 g of $MnSO_4 \cdot 5H_2O$ in 625 ml of water, make the solution ammoniacal, and add 1 l of water containing 50 g of freshly dissolved $(NH_4)_2S_2O_8$. Boil 10 minutes with the addition of sufficient ammonia from time to time to keep the liquid ammoniacal. Allow the precipitate to settle, but, if the supernatant liquid remains cloudy, add 15–25 ml more of the persulfate solution and boil another 10 minutes. Allow the precipitate of MnO_2 to settle, carefully siphon off the supernatant solution, and wash by decantation with four 250-ml portions of hot water. Finally wash twice in the same way with dilute sulfuric acid and then filter through a thin felt of asbestos on a 2-in. filtering disk which is placed in a large funnel. Wash with hot water until free from sulfate, dry at 105° in a clean porcelain dish, grind to pass a 20-mesh sieve, and again dry thoroughly at 105°.

To prepare the absorption tube for sulfur-containing gases, place some ironized asbestos in the bottom of a Midvale tube (see Fig 44C, p. 325) and fill within about an inch of the top with an even distribution of coarse and fine MnO_2; then pack with a plug of glass wool at the top and close with a one-holed rubber stopper carrying capillary tubing. This tube may require conditioning to prevent absorption of CO_2. Place it in the combustion train just behind the drying tower, and run two blank determinations with a high-carbon steel sample. If the carbon result is low, repeat with a high-sulfur steel. One filling should last for several hundred combustions.

K in Fig. 51 represents the weighed tube in which the carbon dioxide is absorbed. A Midvale tube such as is shown in Fig 44 on p. 325 is suitable. It is filled with glass wool at the top and bottom, Ascarite or soda-lime, and the same desiccant as used in J. Fill a newly packed tube with oxygen, weigh, and run a blank with a steel containing a known quantity of carbon. This tube should have as counterpoise a similar tube which is kept near it at all times.

L in Fig. 51 is a gas-flow indicator. Usually concentrated sulfuric acid is used, and the rate at which bubbles of gas pass through it shows whether there is a sufficient supply of oxygen.

Before starting an analysis, observe the following precautions:

1. First test to see if there are any leaks. Close the stopcock at K in Fig. 51, make sure that the valve at A on the oxygen tank is open sufficiently, and then carefully turn the needle valve at B to permit oxygen gas to enter the train. If the apparatus is tight, it can be told by watching the manometer tube at D. If this is not used, leave the stopcock at K open and close the exit at L before opening the valve at B.

2. Allow oxygen to pass through the furnace heated to 1000° for at least 15 minutes, introduce the boat with its lining of Alundum, attach the weighed absorption bulb K, and proceed exactly as in a determination (see below). Weigh the tube again against its counterpoise and, if necessary, continue this heating as in a determination, until the blank is within 0.0005 g. Sometimes it is well to carry out a determination with a Bureau of Standards sample of steel.

Procedure. After the train has been tested and the furnace is at 1000° weigh the absorption tube to the nearest 0.0001 g against its counterpoise. The absorption bulb can be of the Midvale, Nesbitt, Fleming, Newburgh, Vanier, Muehlberg, Richards, or Miller type; all are satisfactory. It is usually assumed that Ascarite is its own drier. Numerous experiments have shown that this is true, but in determining small quantities of carbon it is well to place a little Anhydrone or phosphorus pentoxide at the top of the bulb where the gas leaves the bulb. The same desiccant should be used as was placed in J of Fig. 51. A newly packed bulb should be filled with oxygen to replace the air and allowed to stand in the balance case at least 5 minutes before weighing. The bulb and its filling should not weigh over 100 g, and it is best weighed against another tube of the same kind as counterpoise. A freshly filled

bulb can be used for many determinations but it should be refilled when half the Ascarite contents of the tube have become discolored and nearly white.

Make a V-shaped groove or furrow in the bedding or lining of the boat, which has already been tested by the blank run, and weigh out 1.364 g of ordinary steel or 2.727 g if the carbon content is low. These are factor weights; the value of the fraction $\dfrac{\text{atomic weight C}}{\text{mol. weight } CO_2}$ is 0.2727, and if the sample of steel weighs 1.364 g the percentage of carbon is found by multiplying the weight of CO_2 in grams by 20. Time is saved in a busy laboratory and there is less chance for making an error in calculation if a factor weight or some multiple of it is used.

Before high temperatures were available, it was customary to add an accelerator to the charge to ensure complete combustion. With a furnace capable of a working temperature of 1200°, an accelerator is rarely necessary. Tin is the best accelerator for steels, and when 0.5 g of pure 20–40 mesh tin is added to the top of the charge in the boat, most alloy steels can be burned satisfactorily at 1050°. With very highly alloyed metals such as ferrochrome, tin alone is inadequate and it is necessary to add some pure, hydrogen-reduced iron or 2.727 g of a standard sample of commercially pure iron with known carbon content.

Spread out the sample in the groove, and over this place a suitable cover. Insert the boat into the back end of the combustion tube and, with a clean rod or piece of stainless-steel wire, push the boat forward about 3 or 4 in. and let it warm up there for about a minute before pushing it into the hottest zone of the tube. This procedure is desirable with tubes that are sensitive to thermal shock such as results when a cold boat is placed at once into the hottest part. As soon as the boat has been pushed to the position shown at I in Fig. 51, close the tube and turn on the oxygen slowly until the flow is 300 to 500 ml per minute; the larger flow is used in routine work where many determinations have to be made. The burning of the steel will be shown by a diminished flow of gas at the front end of the train. The combustion should be completed in 4 or 5 minutes. Reduce the flow of oxygen to about 150 ml, and allow 7–10 minutes to sweep out the products of combustion from the furnace. Then close the oxygen valve, disconnect the weighed Ascarite bulb, and let it stand in the balance case at least 2 minutes before weighing. The absorption bulb and its counterpoise, before being placed on the balance pans, should be momentarily opened to the air to bring the pressure inside to that of the air.

Meanwhile withdraw the boat from the furnace by means of a long, heavy wire bent at the end, examine the contents for complete combus-

tion, and place in a desiccator to cool for the next charge. If the fusion appears incomplete, repeat the determination with a higher temperature or with more accelerator. It should be remembered, however, that it is possible to burn out all carbon from the chips without actually fusing them, although this may require 30 minutes or more. Results obtained by pulverizing the residue and reburning are usually less satisfactory than those obtained by starting with a new sample.

Volumetric Method

The apparatus and procedure are the same except that a Meyer tube with 8 to 10 bulbs containing excess $Ba(OH)_2$ is used in place of the weighed Ascarite bulb, the flow of oxygen should be only about 150 ml per minute, and about 25 minutes should be allowed for burning the carbon and sweeping out the furnace. After the combustion, the excess $Ba(OH)_2$ is titrated with standardized HCl to a phenolphthalein end point. The precipitated $BaCO_3$ does not dissolve until the pH is considerably lower than that at which phenolphthalein is decolorized.

Standard Hydrochloric Acid. Mix 8 ml of concentrated HCl with 1 l of water and standardize as described in Chapter XIV, "Acidimetry and Alkalimetry."

Standard Barium Hydroxide. Dissolve 20 g of $Ba(OH)_2 \cdot 8H_2O$ in 1 l of freshly boiled and cooled water. Filter through a large and rapid filter paper in a 5-in. funnel, and keep in a bottle which is provided with a guard tube filled with Ascarite or soda-lime and with a siphon attached to an overflow 80-ml pipet. To standardize this solution, take exactly 80 ml of it, add 25 ml of water and 2 or 3 drops of phenolphthalein indicator solution, and titrate with the standardized HCl until the phenolphthalein is decolorized. Add the acid slowly toward the last so as not to overstep the end point.

Procedure. Weigh out the sample exactly as in the previous method and have it ready to be inserted into the combustion tube. Transfer exactly 80 ml of the standardized $Ba(OH)_2$ solution to the 500-ml heavy Erlenmeyer flask shown in Fig. 53,[1] avoiding contact with the air as much as possible. Immediately insert the rubber stopper which carries the Meyer bulb tube and an inlet tube for the gases from the furnace. Connect the inlet tube to the front end of the combustion train, and omit the gas-flow indicator shown at L in Fig. 51. Support the flask and the Meyer tube in an inclined position so that the liquid in the flask will be forced into the bulb tube by the gas from the furnace. Insert the boat

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[1] From Lundell, Hoffman, and Bright, *Chemical Analysis of Iron and Steel.* The directions are those of the chemists of the United States Steel Corporation.

into the combustion tube, turn on the oxygen gradually, and adjust it during the combustion so that an excess of oxygen gas is always present and gas is constantly bubbling slowly through the absorption gas. Note the appearance of the $Ba(OH)_2$ solution, which will become distinctly turbid in about 5 minutes, showing that oxidation of the sample has begun. If necessary, increase the flow of gas while the sample is burning and then reduce it to the normal rate of about 150 ml per minute. Continue the flow of oxygen about 20 minutes longer, turn off the oxygen, and disconnect the absorption flask.

Hold the flask so that the bulb tube is in a vertical position; as the solution flows into the flask, rinse the bulbs with a stream of cold water which is free from CO_2, and gradually raise the stopper. Finally, when the inside of the bulb tube has been washed with about 25 ml of water and the bulb tube has been raised above the liquid, wash the outside of the tube where it came in contact with the solution. Add 3 drops of phenolphthalein solution and titrate slowly with the standard HCl, agitating the contents enough to ensure complete mixing but avoiding shaking with air. Take the disappearance of color as the end point. Deduct the volume required from that used in the standardization of the

FIG. 53. Flask and bulbs for absorbing CO_2 in $Ba(OH)_2$. The flask and the tube are supported at an angle of 45° to the table, during the combustion of the steel.

Labels on figure: ⅜″, ¼″, 2″, ¼″, 1½″, 11″, ¼″, ⅜″, ¼″, ¼″, Glass Inlet Tube 3½″ long, Rubber Stopper, 3½″, 7½″, 7½″, ½″, 500 ml. Erlenmeyer Flask, 2½″, Rubber Tube, 1½″

Ba(OH)$_2$, and the difference gives the milliliters of HCl equivalent to the carbon of the sample.   One milliliter of 0.1 N HCl = 0.0006000 g C. From the standardization value of the acid the exact value in terms of C can be easily calculated; the solution is approximately 0.1 N.

It is common practice among steel chemists to standardize the HCl solution against a standard steel. This is not to be recommended because, when a sample of steel is certified to contain 0 419 per cent carbon, the values actually obtained by different analysts have sometimes ranged from 0.401 to 0 440, which corresponds to a deviation of about 10 per cent of the actual carbon content. Such an error would be inexcusable in a standardization of HCl against pure Na$_2$CO$_3$. A certified steel should be used to check a method of analysis but never for standardizing solutions to be used in an accurate analysis that takes place as represented by chemical equations

Determination of Graphite

Dissolve 1 g of cast iron in 50 ml of 6 N nitric acid in a 300-ml beaker and heat gently until there is no further evolution of gas. By this means the carbide carbon is dissolved while the graphite is not attacked. Filter the solution through an ignited asbestos filter; wash the residue with hot water, then with a hot 12 per cent solution of potassium hydroxide (d 1.1), followed by hot water, dilute hydrochloric acid, and finally with hot water again until free from chloride. After drying at 110°, transfer the asbestos and graphite into a combustion tube and burn the carbon in a current of pure oxygen as described on p. 348.

Instead of weighing the CO$_2$ formed by combustion or measuring the volume of Ba(OH)$_2$ required to react with the CO$_2$, numerous other procedures have been proposed. Sometimes the BaCO$_3$ is filtered out of contact with air, the filtered precipitate is dissolved in a measured volume of standard acid, and the excess acid is back-titrated with base to a methyl orange end point. The determination has also been based upon the electrical resistance of 200 ml of Ba(OH)$_2$ solution before and after the absorption of CO$_2$, and sometimes the volume of the CO$_2$ gas has been measured. In laboratories where an electric furnace is not available, wet combustion with CrO$_3$, concentrated sulfuric acid, and a copper salt as catalyst has proved successful (see p. 352). One of the late developments has been the simultaneous determination of the CO$_2$ and the SO$_2$ formed from the sulfur in the steel. Several procedures for doing this have been recommended.

Determination of Total Carbon by Wet Combustion

The Chromic-Sulfuric Acid Method

In this method the borings, which should be as fine as possible and free from grease, are treated with a mixture of chromic and sulfuric acids and heated to boiling. Thereby, the iron goes into solution and the carbon is oxidized to carbon dioxide. In spite of a large excess of chromic acid, however, some carbon is likely to escape in the form of hydrocarbons and carbon monoxide, unless precautions are taken. To prevent such losses, Sarnstrom[1] recommended leading the escaping vapors over copper oxide in a combustion tube,[2] 80 cm long, which is heated in a combustion furnace. Many experiments have shown that the method of Särnstrom gives exact results, although objection has been raised to the long combustion tube that is required.

Corleis has succeeded in simplifying the method by showing that a very short combustion tube, filled with copper oxide and heated by a single Bunsen flame, suffices if the sample is covered with a coating of copper during the treatment with chromic and sulfuric acids. In fact, the use of the combustion tube is unnecessary in an ordinary steel analysis, because only 2 per cent of the total amount of carbon present is lost in this case. In the analysis of ferromanganese and similar alloys, however, the use of the hot tube is to be recommended.

Ledebur[3] even found that the results obtained with irons, rich in graphite were a little too high on account of the formation of some sulfur dioxide, but this error
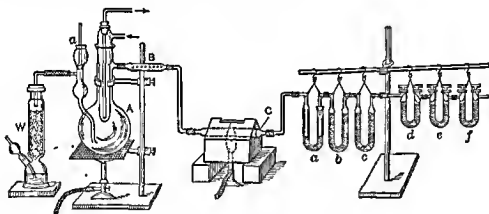
FIG. 54.

can be overcome by passing the gases through chromium trioxide just before they enter the combustion tube.

The apparatus required is shown in Fig. 54 and consists of a Corleis decomposition flask A with condenser.

[1] Särnström, *Berg- und Hüttenm. Ztg*, 1885, 82, and Corleis, *Stahl u. Eisen*, 1894, 581. With ferromanganese the loss amounts to 22.5 per cent of the total carbon, with steel 9 per cent. With ferromanganese the escaping gases contain, besides carbon dioxide and traces of heavy hydrocarbons, 18 per cent methane, 76 per cent hydrogen, 3 per cent oxygen, and 2 per cent carbon monoxide.

[2] A small tube of glass, quartz, or porcelain filled with copper oxide or platinized asbestos.

[3] *Leitfaden für Eisenhütten-Laborat.*

The flask is connected, as shown in the drawing, on one side with a soda-lime tower, W, at the bottom of which is placed a little concentrated caustic potash solution, and on the other side with a system of tubes. The tube B is about 10 cm long and contains chromium trioxide between 2 asbestos plugs. The tube C is 15 cm long, is made of difficultly fusible glass, and filled with granular cupric oxide. It is placed in a little box made of asbestos paper. The tubes a, b, c, d, e, and f are filled exactly as described on p. 347. Tubes a, b, and c are drying tubes, the first contain-

but is used to avoid any chance of carbon dioxide or moisture entering the weighed tubes from the air.

Reagents. 1. A saturated solution of pure chromic acid anhydride CrO_3 free from organic matter. Some samples marked "chemically pure" have been found to contain organic impurity.

2. A solution of copper sulfate made by dissolving 200 g of the salt in 1 l of water.

Procedure. Remove the ground-glass stopper a, and through the opening pour 25 ml of chromic acid solution, 150 ml of copper sulfate solution, and 200 ml of concentrated sulfuric acid into the flask, A, and mix. Heat the mixture in the flask to boiling and keep at this temperature for 10 minutes. Then remove the flame and pass a current of air free from carbon dioxide through the apparatus for 10 minutes at the rate of about 3 bubbles per second. Connect the flask with the tube B, the red-hot copper oxide tube, and with the U-tubes,[1] while continuing the current of air for 5 minutes more. Remove the soda-lime tubes d and e, close, and allow to stand 10 minutes in the balance room. Open for a moment, quickly close, wipe dry with a piece of chamois skin, allow to stand 5 minutes in the balance-case, and then weigh.

By means of this preliminary boiling, traces of organic matter contained in the apparatus are removed.

After weighing the soda-lime tubes, connect them again with the apparatus, open the decomposition flask, and quickly drop in 0.5–5 g of the weighed substance, according to the amount of carbon present,[2] from a weighed glass-stoppered weighing tube, which is subsequently weighed again to determine the amount of sample. Immediately close the flask and heat the copper oxide tube to glowing, after which slowly heat the contents of the flask so that after 15–20 minutes the liquid begins to boil. Keep the solution boiling for 1 or 2 hours while passing a slow current of air through the apparatus. Then remove the flame, and

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[1] Corleis used phosphorus pentoxide for a drying agent, but calcium chloride is satisfactory, cf. p. 325.

[2] For cast iron 0.5 g suffices but for steel from 1 to 2 g and for wrought iron 5 g should be used

pass about 2 l more of air through the apparatus. Then remove the soda-lime tubes and weigh as before.

Since the use of the copper sulfate solution prevents the loss of more than about 2 per cent of the total amount of carbon present, it is evident that the combustion tube can be dispensed with for technical purposes.

Determination of Carbon and Hydrogen in Organic Substances, according to Liebig

(Elementary Analysis)

Principle. The organic substance is burned in air or in oxygen and the products of the combustion are passed over glowing copper oxide, which oxidizes all the carbon to carbon dioxide and the hydrogen to water. The water is collected in a weighed calcium chloride tube or sulfuric acid worm, the carbon dioxide in a weighed vessel which contains either caustic potash solution, soda-lime of 2 per cent moisture content and phosphorus pentoxide, or Ascarite (asbestos impregnated with NaOH). Instead of the gas combustion furnace described here, many prefer to use an electric furnace.

The combustion is performed

  (a) *In an open tube.*
  (b) *In a closed tube.*

Combustion in an Open Tube

Most combustions take place in a tube open at both ends, and usually a furnace heated by gas or electricity and a glass tube are used. The progress of the combustion can be watched through the glass, and a long horizontal column of copper oxide ensures the complete combustion of the carbon. It is possible in many cases to use an electric furnace and carry out the combustion much more rapidly than heretofore. With the electric furnace, it is easier to get a constant temperature sufficient to burn the substance completely, and with soda-lime of the best grade or with Ascarite there is less danger of carbon results being too low. With the Geissler bulb and caustic potash solution, the rapid passage of gas causes volatilization of some of the water too fast to be absorbed by a short drying tube attached to the absorption bulb.

Pregl has shown that it is possible to simplify the process greatly by taking a smaller weight of substance and using a miniature apparatus. This requires a more sensitive balance than is ordinarily used. Pregl's argument that it is easier to get a perfect combustion with a small quantity of substance than with a larger quantity and that it is possible to realize the necessary refinement in weighing, is a perfectly sound one and many chemists are enthusiastic about the results obtained with the

so-called *micro* apparatus. Pregl finds that the technique is easier for a beginner to master. For combustion in the old-fashioned way there are the following

Requirements. (1) An open tube made of difficultly fusible glass which is from 12 to 15 mm wide. The length of the tube depends upon that of the combustion

Fig. 55.

furnace; it must be 10 cm longer than the furnace. (2) 350 g of coarse and 50 g of fine copper oxide. (3) A drying apparatus (Fig. 55 on the left). (4) A calcium chloride tube (Fig 56). (5) A Geissler potash bulb (Fig. 57), or two soda-lime
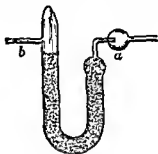
Fig. 56.
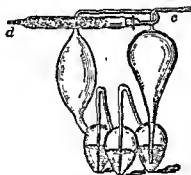
Fig. 57.

tubes or, best of all, an Ascarite bulb. (6) A screwcock. (7) Dry rubber tubing. (8) Two plates of asbestos board to protect the rubber stoppers in the two ends of the tube from the heat of the furnace.

Procedure for the Combustion of Organic Substances Free from Nitrogen, Halogen, Sulfur, and Metals

Preparation and Combustion

1. *Fill the calcium chloride tube* (Fig. 56) from the left side, close with a plug of glass-wool, and fuse together the end of the tube, as shown in the figure.[1] It is more practical to use a calcium chloride tube fitted with ground-glass stoppers. After filling the tube, saturate with carbon dioxide, to react with any free lime in the reagent.

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[1] Or the tube is stoppered and an air-tight seal is made by covering it neatly with sealing wax.

Rub the outside of the tube with a piece of chamois skin, and stopper the two ends with short pieces of rubber tubing each containing a piece of stirring rod. Allow the tube to stand in the balance case for 15 minutes and then weigh without the stoppers. Instead of calcium chloride, other drying agents can be used to advantage (cf. p. 325).

2. *Fill the Geissler bulb* (Fig. 57) with caustic potash solution (2 parts solid KOH in 3 parts of water) as follows: Replace the small soda-lime tube *d* by a piece of rubber tubing, dip *c* into the solution of caustic potash, and fill the bulbs two-thirds full by sucking through the rubber tubing. Then clean the end of the tube *c* with a piece of filter paper, again connect the tube *d* (half filled with soda-lime and the outer half with calcium chloride), and close the two ends with pieces of rubber tubing each containing a piece of stirring rod with rounded ends. Wipe the apparatus with chamois and weigh *without* the stoppers, taking the same precautions as with the weighing of the large calcium chloride tube. A tube filled with solid Ascarite is much better than a Geissler tube with caustic potash. The prolong *d* in Fig. 57 does not retain all the moisture that escapes from the solution during rapid passage of the gas.

3. *The drying apparatus* (Fig. 55, on the left), which serves to free the air and oxygen used for the combustion from carbon dioxide and water vapor, consists of a wash bottle, *D*, containing concentrated caustic potash solution, the soda-lime tube *a*, and the 2 calcium chloride tubes *b* and *c*.

Fig. 58.

4. *The combustion tube* (Fig. 58), both ends of which are fire polished by heating in the blast lamp; after cooling, wash the tube, dry, and fill as follows: First place a short roll, *k*, of copper gauze at the right-hand end of the tube so that 5-6 cm of the tube are left empty. This roll serves as a plug and must, therefore, fit tightly in the tube. Next add a layer of coarse copper oxide, *K*, about 45 cm long, and after this place another plug of copper gauze, *k'*. Finally insert another roll of copper gauze, *d*, about 10 cm long and large enough to fill the tube loosely, so that a space of about 10 cm is left on the right and about 5 cm on the left. Place the tube in the combustion furnace, so that about 5 cm extend beyond the furnace at each end, as shown in Fig. 55. Close the left end of the tube with a tightly fitting rubber stopper through

which a glass tube passes, and connect with the drying apparatus by means of a short piece of rubber tubing. (The tube should be provided with a glass stopcock, which is shown in Fig. 58, *a*, but which is lacking in Fig. 55.) The right end of the tube is left open for the time being.

Pass a slow current of oxygen[1] through the apparatus and light the furnace. At first turn the flame *low and heat the whole tube equally*. Gradually raise the temperature, until, with the tiles covering the tube, the copper oxide is at a dull red heat.

Usually some water condenses in the right-hand end of the tube; expel this by carefully holding a hot tile under the tube. When all the water is removed, and the presence of oxygen can be detected at the right end of the tube (by its igniting a glowing splinter), close this end of the tube with a rubber stopper connected to an open calcium chloride tube. Now turn down the burners and discontinue the oxygen current. *Extinguish all the flames after some time except those* under the right half of the tube.

While the tube is cooling, weigh the calcium chloride tube and the potash bulb (or soda-lime tubes), replacing the stoppers immediately after the weighing, and weigh 0.15–0.2 g of the substance into a porcelain boat.

If the substance is a difficultly volatile oil weigh it from a small glass tube open at one end. If it is readily volatile, blow a small bulb on a piece of narrow glass tubing and draw out the open end into a small capillary tube; weigh this, heat the bulb, and *introduce the capillary into the liquid to be analyzed*, so that the liquid rises in the bulb as it cools. Then turn the bulb so that the capillary lies in a horizontal position, heat slightly to expel a little liquid that adheres to the sides of the tube, melt the end together, and again weigh the tube. Take care that there is no liquid in the capillary. Everything is now ready for the combustion. Remove the stopper from the left (and now cold) end of the combustion tube; remove the long copper roll by means of a piece of wire with a hook in the end of it; place the boat with the substance in it in the tube and the copper roll right after it. Make connection with the drying apparatus on the left and with the absorption tubes on the right, as is shown in Fig. 55. If the substance is a liquid, place the bulb containing it so that its capillary is pointed towards the left, and with a volatile liquid break off the end of the capillary

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[1] The oxygen must be free from hydrogen. Commercial oxygen often contains hydrogen; if so, it is necessary to pass the gas through a "preheating" furnace before using it. Cf. p. 314.

with a file just before introducing it into the combustion tube. Close the stopcock between the tube and the drying apparatus, connect the latter with an air-gasometer, and open wide the stopcock in the drying apparatus and that between the drying apparatus and the combustion tube just enough to permit 2, or at the most 3, bubbles of gas per second to pass through the apparatus. Light the two outer burners on the left and heat the copper oxide spiral d (the copper was changed to the oxide by the ignition in oxygen) just to redness. Gradually heat the tube from right to left, taking care that the gas evolution is never greater than 4 bubbles per second through the potash bulb; this can be easily regulated by means of the stopcock or by turning the gas-burners. When the contents of the entire tube have been brought to redness, with the tiles in place, and the boat is empty, the combustion is usually complete. It is well, however, to pass oxygen through the tube until the gas can be detected at the right-hand end of the combustion train (a glowing splinter ignites at n).[1] Then turn down the flames and pass a current of air through the apparatus until the oxygen is completely expelled. A little water always collects in the front (right) end of the tube, and this must be driven over into the calcium chloride tube by holding a hot tile under it. Now remove the calcium chloride tube and the potash bulbs, wipe off with a piece of chamois skin, allow to stand in the balance room for 20 minutes, and weigh without the stoppers. The gain in weight represents the amount of water and carbon dioxide respectively, and from this the amount of hydrogen and carbon can be calculated.

Remark. The combustion may be accomplished as described for the determination of carbon in steel but with the following precautions:

1. Place plugs of copper gauze and a layer of copper oxide in the front end of the furnace as described above, but use less copper oxide because of the shorter furnace. Before the combustion beat in oxygen to convert the copper to copper oxide, as described above, and to burn any dust in the tube.

2. Do not use more than about 0.1 g of substance, and cover it with about 2 g of copper oxide powder. Use a slower stream of oxygen as only about 12 ml is required for complete combustion.

3. Have the combustion tube well cooled before introducing the boat with the substance and beat the front end of the tube first by moving the tube so that the part containing the boat is outside the furnace. When the front end of the tube is hot, place the tube in its normal position.

4. Use the absorption train as described above, but substitute a Midvale or Fleming tube filled with Ascarite as described on p. 347.

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[1] To prevent moisture from getting into this tube from the air, it is well to connect it with an unweighed calcium chloride tube.

Determination of Carbon and Hydrogen in Nitrogenous Organic Substances

By the combustion of many organic substances containing nitrogen, especially nitroso and nitro compounds, oxides of nitrogen are formed which are partly absorbed in the calcium chloride tube and partly in the potash bulb, so that if such substances were analyzed according to the previous process, both the carbon and hydrogen results would be too high. If, however, a reduced copper spiral is introduced in the front (right) end of the combustion tube, this serves to reduce the oxides of nitrogen to nitrogen itself, and, as nitrogen is not absorbed, correct results will be obtained.

Prepare the copper spiral by rolling together a piece of copper gauze about 10 cm wide, making it as large as will conveniently pass into the combustion tube. Heat the spiral till it glows by holding it in a large gas flame, and while still hot drop it into a test tube containing 1 or 2 ml of methyl alcohol. The alcohol quickly boils away, but some of it is oxidized to aldehyde by the hot copper oxide, which is reduced completely to bright metallic copper. Take out the spiral with a pair of crucible tongs and dry by quickly passing it through a flame a few times, and while still warm introduce it into the front end of the combustion tube, which has been previously burned out as described in the previous analysis.

To carry out the combustion, close the stopcock between the combustion tube and the drying apparatus (Fig. 55), insert the substance into the tube, and first heat the copper oxide spiral at d and then the reduced spiral at the other end of the tube. Then, beginning at k (Fig. 58), light one burner after another, until finally the entire contents of the tube are heated to dull redness and no more bubbles escape through the potash bulb. Now for the first time open the stopcock somewhat and pass oxygen through the tube until it can be detected at n, by a test with a glowing splinter. Then gradually turn down the flames, replace the oxygen by air, and complete the analysis as in the previous case.

Substances hard to burn are treated somewhat differently. First of all fill the back end of the combustion tube (Fig. 58) with the aid of the funnel T (Fig. 59), with fine, granular, but not pulverized, copper oxide, and ignite this in a stream of oxygen. Replace the oxygen by air and allow the tube to cool until it can be held in the hand. Next transfer the fine, granular copper oxide to the small flask K, Fig. 60, and close the flask by inserting a tinfoil-covered cork, fitted with a calcium chloride tube. While the copper oxide in the flask is becoming perfectly cold, weigh the substance to be analyzed into the glass-stoppered

mixing tube M, Fig. 61. Transfer from one-sixth to one-fifth of the copper oxide in the flask to the mixing tube, stopper, and shake the contents well, whereby the substance becomes intimately mixed with the copper oxide to which it adheres. Transfer the mixture back to the combustion tube, and shake the mixing tube repeatedly with small
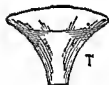
FIG. 59.   FIG. 60.   FIG. 61.

portions of the remaining copper oxide in the flask until finally it can be assumed that all the substance has been transferred to the combustion tube. Then carry out the combustion in the usual manner.[1]

Combustion of Organic Substances Containing Halogens

The analysis is conducted exactly the same as for nitrogenous substances, except instead of a reduced copper spiral one of silver is used to keep back any halogen. The silver spiral should not be heated to redness, but only to about 180-200°. If a silver spiral is not at hand, use a long copper spiral, its end reaching outside the furnace.

[1] For another method of conducting a combustion in an open tube, consult M. Dennstedt, Z. anal. Chem., 40, 611 (1903).

Combustion of Organic Substances Containing Sulfur

Sulfur compounds cannot be burned in a tube containing copper oxide, for the sulfur dioxide escapes and is partly absorbed by the water in the calcium chloride tube and partly in the potash bulb, so that absolutely worthless results are obtained. Instead of the long layer of copper oxide, use one of ignited lead chromate; this oxidizes the sulfur dioxide to sulfur trioxide, forming difficultly volatile lead sulfate which remains in the tube. When lead chromate is used, the combustion must take place at a lower temperature than with copper oxide, for the chromate melts easily, and by adhering to the glass is likely to cause the tube to break.

Combustion of Organic Substances Containing Metals

If the substance contains alkalies, alkaline earths, or cadmium, a part of the carbon will remain in the tube as carbonate. In this case mix the substance in the boat with a mixture of 10 parts of powdered lead chromate and 1 part of potassium chromate, and conduct the combustion as when sulfur is present.

Dumas' Method for Determining Nitrogen in Organic Substances

This determination should really be discussed in Chapter XIX, but it will be described here on account of its being an analysis by combustion.

Principle. The substance is burned in a combustion tube, free from air, which contains copper oxide and copper spirals exactly as in the determination of the hydrogen and carbon in substances containing nitrogen, but in this case the volume of the nitrogen evolved is *measured.*

Procedure. This determination may be carried out in either a closed or an open tube.

(a) Determination of Nitrogen in a Closed Tube

The necessary apparatus is shown in Fig. 62. The combustion tube is closed at one end and is about 75 cm long. It contains at M a layer of magnesite or of manganese carbonate 15 cm long, in pieces about the size of a pea, followed by a loose plug of ignited asbestos and then a 10-cm layer of coarse copper oxide, S. Add the substance at a in a boat and mix with powdered copper oxide by means of a spiral wire (cf. p. 360), then add a layer of coarse copper oxide[1] about 40 cm long and finally the reduced copper spiral (prepared as described on p. 359). Place the tube in a combustion furnace and connect as shown in the figure with an azotometer,[2] which contains mercury to a little above

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[1] The copper oxide must be previously ignited, as described on p. 359.

[2] H Schiff, *Ber.*, 13, 885.

the lower end of r, and a liberal amount of caustic potash solution (300 g KOH dissolved in a liter of water).

Begin the analysis (with the leveling bulb low and the stopcock of the azotometer open) by heating the left half of the magnesite layer, whereby the air in the tube is expelled by the carbon dioxide and passes through the azotometer. From time to time make a test to see whether
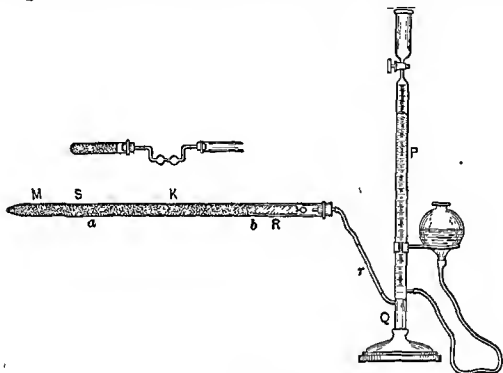
FIG. 62.

all the air has been expelled. Raise the leveling bulb, and close the stopcock with the azotometer tube completely filled. If all the air has been replaced by carbon dioxide gas, the bubbles of gas will all be absorbed by the caustic alkali. When this occurs put out the flame under M. Heat the tube first at R and light the burners one after another toward the left until about three-quarters of the layer of coarse copper oxide is heated to a dull redness. Then heat the tube at S and continue the process as in an ordinary combustion until the whole tube (with the exception of the part where the magnesite is found) is heated to a uniform temperature and finally no more nitrogen is evolved.

The heating must be accomplished so that there will be a slow but steady evolution of nitrogen. When the combustion is complete, heat the magnesite layer once more and expel all nitrogen remaining in the tube. As soon as the volume of the gas in the azotometer remains constant, measure the nitrogen.

For this purpose remove the azotometer together with the connecting piece of rubber tubing from the combustion tube and close the tubing by means of a pinchcock. Set the apparatus aside for at least 30 minutes at a place where a uniform temperature prevails, then raise the leveling tube until the solution in it stands at exactly the same height as that in the tube. Read the volume of nitrogen, the thermometer, and the barometer.

The weight of the nitrogen present is computed as follows:

Assume a g of the substance used for the analysis and V ml of nitrogen obtained at $t°$ and B mm barometric pressure. In order to obtain the weight of the nitrogen, its volume must first be reduced to 0° and 760 mm pressure. If the gas had been measured over pure water the formula

$$V_0 = \frac{V(B_0 - w)\cdot 273}{760(273 + t)}$$

would hold, in which B_0 represents the observed barometer reading reduced to a temperature of 0° and w is the tension of water vapor measured in millimeters of mercury. The nitrogen, however, was not measured over pure water but over a solution of potassium hydroxide, and the vapor tension of this solution is less than that of pure water. In fact, with potassium hydroxide of the concentration used, the diminution of the vapor tension as compared with pure water almost exactly compensates the correction which would be applied in reducing the barometer reading to 0°. Consequently the following formula holds with sufficient accuracy:

$$V_0 = \frac{V(B - w)\cdot 273}{760(273 + t)}$$

As 1 ml of nitrogen at 0° and 760 mm has been found to weigh 0.0012506 g,[1] then V_0 ml of nitrogen will weigh

$$0.0012506 \times V_0 \text{ g}$$

and the substance contains $\dfrac{0.12506 \cdot V_0}{a}$ per cent of nitrogen.

If the value of V_0 is inserted in this last equation, and the constant values are united, it becomes

$$x = 0.04493 \frac{V(B - w)}{(273 + t)\cdot a} = \text{per cent } N$$

_____

[1] Cf. " Nitrogen " in Chapter XIX.

(b) *Determination of Nitrogen in an Open Tube*

The determination is carried out in practically the same way as before, except that the carbon dioxide is generated outside of the tube. If the combustion tube of Fig. 62 is imagined cut off at M and connected by means of the two-bulbed tube with a long test tube, as shown in the upper part of the figure, the apparatus necessary for this determination will be seen.

The long test tube contains sodium bicarbonate, and it is covered with a piece of copper gauze in order that it may be heated more uniformly.

At S is a long copper oxide spiral; this is followed by a copper boat containing the substance mixed with powdered copper oxide, then the long layer of coarse copper oxide, and finally the reduced copper spiral. After the connection with the azotometer has been made, heat the tube containing the sodium bicarbonate and remove the air from the combustion tube by means of the carbon dioxide evolved. The greater part of the water that is simultaneously set free collects in the two-bulbed tube. Otherwise the procedure is exactly the same as before.

Remark. The advantage of this method over the former lies in the fact that the combustion tube can be used for a large number of nitrogen determinations without refilling it each time.

With difficulty combustible substances the author prefers to work with the closed tube, for in this way it is possible to get a very intimate mixture of the substance with the powdered copper oxide.

OXALIC ACID, $H_2C_2O_4 \cdot 2H_2O$. Mol. Wt. 126.07

Forms: Calcium Oxide, CaO, and Carbon Dioxide, CO_2

Determination as Calcium Oxide

Treat the neutral solution of an alkali oxalate with a few drops of acetic acid, heat to boiling, and precipitate with boiling calcium chloride solution. After allowing to stand for 12 hours filter off the precipitate, wash with hot water, and treat the precipitate as described for the determination of calcium (cf. pp. 244, 265, 266).

BORIC ACID, H_3BO_3. Mol. Wt. 61.84

Determination as Boron Trioxide, B_2O_3, by the Method of Rosenbladt-Gooch[1]

Principle. Alkali and alkaline-earth borates, on being distilled with absolute methyl alcohol (free from acetone) and acetic acid, give up all their boron in the

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[1] *Z. anal. Chem.*, 27, 18, 364 (1887).

form of methyl borate, a liquid which boils at 65°. If the methyl borate is brought into contact with a weighed amount of lime in the presence of water, it is completely saponified:

$$B(OCH_3)_3 + 3H_2O = 3CH_3OH + B(OH)_3$$

The boric acid set free combines with the lime to form calcium borate. If the paste of water and lime is evaporated to dryness, the gain in weight, therefore, represents the amount of B_2O_3.

Procedure. Ignite about 1 g of the purest lime[1] obtainable to constant weight over the blast lamp, and transfer as much of it as possible to the dry Erlenmeyer flask (Fig. 63) which serves as a receiver. Place the crucible, with some of the lime adhering to it, in a desiccator and set aside for the present.

Slake the lime in the flask by carefully adding about 10 ml of water. Connect the flask with the distillation flask as shown in the figure.[2]

Treat the aqueous solution of the alkali borate (containing not more than 0.2 g B_2O_3) with a few drops of either litmus or lacmoid solution, and add hydrochloric acid drop by drop until the solution turns red. Then add 1 drop of dilute sodium hydroxide and a few drops of acetic acid.[3] Add the faintly acid solution by means of the funnel T to the pipet-shaped retort, R, of about 200-ml capacity. Rinse out the funnel 3 times with 3-ml portions of water and close the stopcock. Distil off the liquid by placing R in a paraffin bath at not over 140°, and collect the distillate in the Erlenmeyer flask containing the lime. When all the liquid has distilled over, lower the paraffin bath and, after R has cooled somewhat, add 10 ml of methyl alcohol (free from acetone)
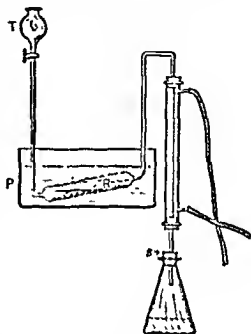
Fig. 63.

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[1] Instead of lime, Gooch and Jones use 4–7 g of sodium tungstate fused with about 0.1 g WO_3 in a platinum crucible to expel any carbonic acid. The fused mass is cooled and weighed.

[2] To permit the escape of air from the flask, make a cut in the side of the cork stopper, at s.

[3] It is also necessary to neutralize the greater part of the alkali with hydrochloric acid and then the last of it with acetic acid. If all the alkali were neutralized with acetic acid, little or none of the boric acid would pass over into the receiver during the subsequent distillation with alcohol.

through the funnel and again distil off the liquid in R. Repeat this process 3 times. Then add 2–3 ml of water to the retort, a few drops of acetic acid until the liquid becomes distinctly red again,[1] and repeat the distillation with 10 ml of methyl alcohol 3 times more. At the end of this time all the boric acid will be found in the receiver. When the distillation is over, the retort should be removed from the paraffin bath by lowering the bath. If this is not done, the retort is likely to break when the paraffin solidifies. Shake the stoppered flask thoroughly and allow to stand for an hour or two to make sure that all the methyl borate is saponified. Then pour the contents of the receiver into a 200-ml platinum dish and evaporate on the water bath to dryness at as low a temperature as possible. During this process the alcohol must not be allowed to boil under any circumstances. Then, in order to remove the small amount of lime that remained adhering to the sides of the flask, add a few drops of dilute nitric acid to the receiver, and, by carefully inclining the flask, wet its entire inner surface with the acid, after which wash the contents into the platinum dish and evaporate to dryness again. This time the water in the bath may boil, as there is now no danger of losing the boric acid, all the alcohol having been removed by the first evaporation. Gently ignite the residue in the dish over a small flame to destroy the calcium acetate that was formed by the excess of acetic acid added. Allow to cool, and transfer by means of a little water to the crucible in which it was originally weighed. Dissolve the dark-colored lime remaining on the sides of the dish in a little nitric or acetic acid and wash into the crucible. Evaporate the contents of the crucible to dryness on the water bath and, with the cover upon it, ignite the crucible at first gently and finally more strongly until a constant weight is obtained. The increase in weight represents the amount of B_2O_3.

Remark. This method affords faultless results, even in the presence of considerable amounts of other salts. Free halogen hydride or sulfuric acid must not be present, for these acids form esters with the methyl alcohol and distil over with boric acid, with which they would be weighed. Instead of using lime in the receiver, the methyl borate can be distilled into a dilute solution of ammonium carbonate, and the latter evaporated with slaked lime in a platinum dish immediately after the distillation.

If one possesses a large platinum crucible (with a capacity of 80–100 ml), the first evaporation can take place in this and it is then advisable to place the crucible within a ring-shaped copper or tin tube through which steam passes. In this way the calcium acetate does not creep up over the sides of the dish, and there is no danger of any bumping.

[1] By the repeated distillation, the contents of the retort become alkaline, as shown by the blue color of the solution.

Determination of Boric Acid in Silicates, Enamel, etc.

Fuse the finely powdered substance with 4 times as much sodium carbonate, extract the melt with water and evaporate the aqueous solution containing the boric acid[1] to a small volume, make acid with acetic acid, and, without regard to any separation of silica, transfer the solution to the Gooch retort and analyze as above directed.

Remark. This determination can be performed in the presence of fluorine provided that acetic and not nitric acid is used to set free the boric acid; but, for that matter, it is never advisable to use nitric acid and it is not permissible when chlorides are present. A convenient titration method will be described in Chapter XIV.

Determination of Boric Acid in Mineral Waters

If the water contains considerable boric acid (0.1 g or more of B_2O_3 in a liter), evaporate a weighed amount (from 200 to 300 ml) to a small volume,[2] filter off the precipitated calcium and magnesium carbonates, concentrate the filtrate, make slightly acid with acetic acid, and analyze as described on p. 365.

If the water contains only a little boric acid, as is usual, a large amount must be taken for the determination. Evaporate 10–15 l in a large porcelain dish to about 1 l,[2] filter off the deposited salts (these never contain any borate), wash thoroughly with hot water, and evaporate the filtrate and washings on the water bath until a moist residue is obtained. If this residue does not amount to more than 5 or 6 g redissolve it in water, make acid with acetic acid, transfer to the Gooch retort, and distil as described on p. 366. Usually a larger residue is obtained, which can be conveniently analyzed directly; in this case the boric acid is extracted from it. For this purpose make the residue acidic with a little hydrochloric acid, thoroughly stir with absolute alcohol, and by means of more of the latter transfer it to a flask, cork up, and allow to stand 12 hours with frequent shaking. The boric acid will then be found in the alcoholic solution. Filter off the residue, wash with 96 per cent alcohol, dilute largely with water, add 1 g of sodium hydroxide, distil off the alcohol (see Remark on p. 368), and evaporate the liquid until a moist residue is obtained. Make this again acidic with hydrochloric acid and repeat the above extraction with alcohol, and subsequent distillation of the alcohol, after the addition of water and 1 g of sodium hydroxide. If the residue now obtained is not too large, ignite gently

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[1] Sometimes the insoluble residue contains appreciable amounts of boric acid. In the method given in Chapter XIV, this fact will be taken into consideration.

[2] If the water reacts alkaline, evaporate it at once; otherwise add enough sodium carbonate solution to make it alkaline.

to destroy the organic matter; after extracting with water, filter off the carbonaceous residue and make the filtrate acidic with hydrochloric acid. Then add sodium hydroxide till barely alkaline and just enough acetic acid to make the solution react acid again. Analyze the solution thus prepared as described on p. 365.

Remark. Unless a large amount of water and the sodium hydroxide are added, some of the boric acid will be volatilized with the alcohol. It is always best to test the alcoholic distillate for boric acid as follows: extract a few pieces of turmeric root with alcohol; place 2–3 drops of the yellow solution in a porcelain dish; add the alcoholic solution to be tested for boric acid and a few drops of acetic acid. Dilute with water and evaporate to dryness on the water bath. According to F. Henz, if as much as 0.001 mg of boric acid is present, a faint but distinct coloration will be evident, while the presence of 0.02 mg will cause a strong reddish brown coloration, which on being treated with sodium hydroxide is turned to the characteristic blue-black color.

If boric acid is found in the alcoholic distillate, it must be again treated with water and sodium hydroxide, and the alcohol once more distilled off.

MOLYBDIC ACID, $H_2MoO_4 \cdot H_2O$. Mol. Wt. 179.98

The determination of molybdenum present as molybdic acid has already been considered on p. 113.

TARTARIC ACID, $H_2C_4H_4O_6$. Mol. Wt. 150.09

The composition of free tartaric acid as well as that of the tartrates is determined by an elementary analysis; see pp. 354 et seq.

META- AND PYROPHOSPHORIC ACIDS

These acids are changed to phosphoric acid and determined as described on p. 370.

IODIC ACID, HIO_3. Mol. Wt. 175.93

Form: Silver Iodide, AgI

For the determination of iodic acid as silver iodide, make the solution of the alkali iodate acid with sulfuric acid, and add sulfurous acid until the solution, which at first becomes yellow on account of the separation of iodine, is again colorless. After this add an excess of silver nitrate and a considerable amount of nitric acid. Heat the solution to boiling, and determine the precipitated silver iodide as described on p. 297.

It is not permissible to change the iodate to iodide by ignition, for the decomposition takes place at a temperature above that at which the

iodide itself begins to volatilize. The transformation is, therefore, not quantitative. This is especially true of sodium iodate, which is changed to iodide only upon heating to a white heat. Potassium and silver iodates are much more readily decomposed, but even then some iodide is lost. Both iodic and periodic acids may be more accurately determined by a volumetric process (see Chapter XV, "Iodimetry").

For the determination of the metal present in an iodate, first change it to the chloride by repeated evaporation with concentrated hydrochloric acid:

$$KIO_3 + 6HCl = KCl + 3H_2O + 2Cl_2 + ICl$$
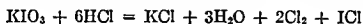
GROUP IV OF ANIONS

PHOSPHORIC, ARSENIC, ARSENIOUS, THIOSULFURIC, CHROMIC, VANADIC, AND PERIODIC ACIDS

PHOSPHORIC ACID, H_3PO_4. Mol. Wt. 98.00

Forms: Magnesium Pyrophosphate, $Mg_2P_2O_7$; Ammonium Phosphomolybdate, $(NH_4)_3PO_4 \cdot 12MoO_3$; Phosphomolybdic Anhydride, $P_2O_5 \cdot 24MoO_3$

1. Determination as Magnesium Pyrophosphate, according to B. Schmitz

Formerly it was the usual practice to precipitate phosphoric acid in the cold with "magnesia mixture" and ammonia, but according to the experiments of Neubauer[1] and of Gooch[2] it is evident that it is very difficult to obtain a pure precipitate of magnesium ammonium phosphate in this way; sometimes it is contaminated with $Mg_3(PO_4)_2$ and sometimes with $Mg(NH_4)(PO_4)_2$. If, however, the precipitation takes place in a hot solution, a very pure, coarsely crystalline precipitate of $Mg(NH_4)PO_4 \cdot 6H_2O$ is obtained.[3]

Procedure. To 50 ml of a neutral solution containing 0.1–0.5 g of P_2O_5 add a few drops of dilute hydrochloric acid, an excess of "magnesia mixture,"[4] 5 g of ammonium acetate, and a little phenolphthalein solution. Heat nearly to boiling; run in from a buret 1.5 N ammonia, while constantly stirring, until a turbidity forms. Stir till the precipitate is crystalline and then continue adding the ammonia until a red coloration is obtained from the indicator. Allow the solution to cool completely, add one-fifth of its volume of concentrated ammonia, and let stand at least 4 hours. Wash the precipitate 3 times by decantation with 1.5 N ammonia, then transfer to a filter, and wash free from chloride. Finally moisten the precipitate with a saturated solution

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[1] H. Neubauer, Z. angew. Chem., 1896, 439.

[2] F. A. Gooch, Z. anorg. Chem., 20, 135.

[3] B. Schmitz, Z. anal. Chem., 65, 46 (1924); K. K. Järvinen, Z. anal. Chem., 43, 279 (1904), 44, 333 (1905); G. Jórgensen, Z. anal. Chem., 45, 278 (1906).

[4] The "magnesia mixture" is prepared, according to Schmitz, by dissolving 55 g of magnesium chloride, $MgCl_2 \cdot 6H_2O$, and 105 g of ammonium chloride in water, adding a little hydrochloric acid, and diluting to a volume of 1 l. For 0.1 g of P_2O_5, use 6 ml of this solution.

of ammonium nitrate in $1.5\,N$ ammonia, dry, ignite, and weigh as described on p. 258. It is best to use a filtering crucible and an electric oven.

If the weight of the precipitate is p, then the corresponding weights of H_3PO_4 and P_2O_5 are

$$\frac{2H_3PO_4 \cdot p}{Mg_2P_2O_7} = \text{weight } H_3PO_4 \quad \text{and} \quad \frac{P_2O_5 \cdot p}{Mg_2P_2O_7} = \text{weight } P_2O_5$$

The above method for the precipitation of phosphoric acid is not applicable when the substance contains alkaline earths or heavy metals. Under these conditions the phosphoric acid should be precipitated first as ammonium phosphomolybdate and the phosphoric acid in this precipitate determined by one of the following methods.

2. Determination of Phosphoric Acid as Magnesium Pyrophosphate after Previous Precipitation as Ammonium Phosphomolybdate

This method, first proposed by Sonnenschein, has experienced, in the course of time, a great many modifications.[1] It is always applicable when the phosphoric acid is present as orthophosphate.

Titanium, zirconium, quinquevalent vanadium, and quinquevalent arsenic interfere, all precipitating with the phosphorus. Titanium and quinquevalent vanadium also prevent complete precipitation. Cain and Tucker[2] have shown that the interference of vanadium can be prevented by reducing it to the quadrivalent condition and precipitating at 20°, and by precipitating at this low temperature the interference of arsenic is overcome.

Principle. If a solution containing phosphoric acid in the presence of ammonium nitrate and sufficient nitric acid is treated with an excess of ammonium molybdate and heated to 60-70°, all the phosphoric acid is precipitated as yellow ammonium phosphomolybdate. When dried at room temperature over $CaCl_2 \cdot 2H_2O$, the precipitate corresponds to the formula — $(NH_4)_3PO_4 \cdot 12MoO_3 \cdot 3H_2O$ if it has been thoroughly washed with water or with potassium nitrate solution[3] and to $(NH_4)_3PO_4 \cdot 12MoO_3 \cdot HNO_3 \cdot 2H_2O$ if washed with dilute nitric acid. It always contains, when sufficient molybdic acid is present, 24 moles of MoO_3 to 1 mole of P_2O_5.

In the analysis of minerals, appreciable quantities of phosphoric acid are likely to be found in the dehydrated silica especially when titanium, zirconium, thorium, or tin is present. Some of this phosphorus will be lost and counted as SiO_2 if, in testing the purity of the silica, considerable sulfuric acid is used with the hydrofluoric acid and the acid is subsequently volatilized at a high temperature. In fusions with alkali pyrosulfate, some phosphoric acid is volatilized

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[1] Cf Woy, *Chem. Ztg.*, 21, 442; Hundeshagen, *Z. anal. Chem.*, 28, 164; Eggertz, *J. prakt. Chem.*, 79, 406; v Juptner, *Oesterr. Z. Berg-Hüttenw.*, 1894, 4711; McCandless and Burton, *Ind. Eng Chem.*, 16, 1267 (1924); McNabb, *J. Am. Chem. Soc.*, 50, 300 (1928).

[2] *J. Ind Eng. Chem.*, 5, 647 (1913).

[3] M. Ishibashi, *Mem. Coll. Sci.*, A, 12, 135 (1929).

Very small quantities of phosphoric acid in the presence of considerable copper, nickel, chromium, etc., are often concentrated by adding a little iron or aluminum and precipitating with ammonia. Phosphoric acid can also be precipitated with zirconium (cf. p. 182). Phosphoric acid can be separated from iron, nickel, cobalt, titanium, zirconium, chromium, etc., by precipitating these elements as hydroxides in the presence of excess NaOH. The same end is accomplished by fusion with alkali carbonate, which converts the phosphoric acid into water-soluble alkali phosphate; if much calcium phosphate is present it is necessary to add silica to the flux in order to obtain all phosphoric acid as soluble phosphate.

Arsenic acid forms with ammonium molybdate a compound which is analogous to ammonium phosphomolybdate but the arsenic precipitate does not form readily if the temperature is below 70°. If arsenic is reduced to the trivalent condition, it can be volatilized as AsCl₃ by boiling with HCl or HF; platinum vessels must be used in the last case. Such treatment also serves to remove quadrivalent germanium. A fairly satisfactory separation of phosphoric acid from tungsten, quinquevalent vanadium, or sexivalent molybdenum can be obtained by precipitation with magnesia mixture in an ice-cold ammoniacal solution containing tartrate or citrate.

Other separations can be accomplished by depositing metals such as iron, copper, nickel, chromium, or molybdenum electrolytically on a mercury cathode, by precipitating with iron or copper with cupferron in the presence of considerable HCl, or by extracting ferric chloride with ether.

For the complete precipitation of phosphoric acid with ammonium molybdate, a considerable excess of molybdate is necessary; the solution after the addition of the reagent should contain 5 to 8 per cent of HNO₃, and more than 5 per cent of NH₄NO₃. Precipitation is retarded by hydrochloric, sulfuric, or hydrofluoric acid, excessive quantities of the ammonium salts of these acids, quadrivalent or quinquevalent vanadium, titanium, zirconium, and many organic compounds. Satisfactory analyses can be made in solutions which are 1.2 N in HCl or 18 N in H₂SO₄ provided that about twice as much reagent is used as is ordinarily required and a longer precipitation period allowed. In the absence of retarding agents, it is customary to add at least 1.5 g more of MoO₃ than is required theoretically. In determining small quantities of phosphorus this may be more than 100 times the quantity theoretically required.

Various formulas have been used for preparing the ammonium molybdate reagent. For the last fifty years, the reagent most used in the United States is a solution containing, besides the ammonium molybdate, considerable ammonium nitrate and free nitric acid. When this reagent is used, the solution analyzed should be nearly neutral as sufficient nitric acid is present to provide for complete precipitation, but if the solution to be analyzed contains considerable free acid or if it is basic in reaction the reagent will be incomplete. The acid molybdate reagent, however, is not very stable and stains the fingers if spilled upon them. For that reason, many chemists prefer to use a neutral or slightly ammoniacal solution of ammonium molybdate. Three formulas for preparing the reagent will be given. The first is the reagent recommended by Blair which is strongly acidic and, according to chemists of the National Bureau of Standards, is still most used. It has been used at the Massachusetts Institute of Technology for over forty years. The second formula has been recommended by the American Society for Testing Materials; it is similar to the third formula, which is recommended by C. M. Johnson.

Personally, the writer prefers the third formula, but some of his colleagues like the first one, and experience has shown that confusion will result if the stockroom uses more than one formula. In carrying out this analysis, the student should find out which formula comes nearest to that used in the laboratory in which he is working.

Acid Ammonium Molybdate Solution. Mix 100 g of pure MoO_3, or 118 g of $(NH_4)_6$-$Mo_7O_{24} \cdot 4H_2O$ (85 per cent MoO_3), with 400 ml of water, and dissolve it in 80 ml of strong NH_4OH (d 0·90 or about 15 N) with stirring. Filter if necessary, cool and pour very slowly, while stirring, into 715 ml of 6 N HNO_3. Add 1 or 2 drops of 10 per cent NH_4HPO_4 solution and allow to stand at least 12 hours. Decant off the clear liquid or filter through an asbestos pad as required for use.

Ammonium Molybdate (A.S.T.M. Formula). Take 65 g of pure $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 225 g of NH_4NO_3, 15 ml of concentrated NH_4OH, and 600 ml of water. Stir and heat gently. When the crystals have dissolved, filter (without washing) and dilute to 1 l.

Ammonium Molybdate (Johnson's Formula). Digest 55 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and 50 g of NH_4NO_3 with 18 ml of 15 N NH_4OH and 20 ml of water. Stir, dilute to about 700 ml with water, and heat for 30 minutes with occasional stirring until all salts have dissolved. Dilute to 1 l, let stand over night, filter, but do not wash the residue.

Procedure. To 50 ml of solution containing 0.1 g of P_2O_5 or less, carefully add 6 N ammonium hydroxide until the solution is neutral to litmus.[1] Add a few drops of 6 N nitric acid, heat the solution to about 65°, and add 75 ml of ammonium molybdate reagent. Keep the solution at this temperature for half an hour, filter, and wash once by decantation with an acid solution of ammonium nitrate[2] and at least 6 times on the filter. When the washing is complete place the flask containing the bulk of the precipitate under the funnel and allow 6 N ammonium hydroxide solution to drop upon the upper edge of the filter from a buret, until enough has been added to dissolve all the precipitate on the filter paper and that in the flask. Rotate the contents of the flask from time to time and avoid using an unnecessary excess of ammonia. Wash the filter paper thoroughly with hot water. The volume should not exceed 100 ml at this point. Drop a piece of sensitive litmus paper into the solution and add 6 N hydrochloric acid, with constant rotation of the flask, until the litmus paper changes to a violet verging on the blue rather than the red. Pay no attention to precipitation of yellow ammonium phosphomolybdate at this point. Add 10 ml of magnesia

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[1] These directions assume that the *acid solution* of ammonium molybdate (formula 1) is used as reagent. If either of the other two solutions is used, omit the neutralization with ammonia and, instead of adding a few drops of nitric acid, make sure that the equivalent of 6 to 10 g of HNO_3 (16 to 27 ml of 6 N HNO_3) is present together with at least 6 g of NH_4NO_3.

[2] Mix 100 ml of 6 N ammonium hydroxide with 325 ml of 6 N nitric acid and dilute with 100 ml of water.

mixture[1] and heat almost to the boiling point.   Add 2–3 drops of phenol-
phthalein indicator, and neutralize with 1.5 N ammonium hydroxide
until the solution is colored pink by the indicator.   Cool, add one-fifth
of the solution's volume of concentrated ammonium hydroxide, and allow
to stand for at least 4 hours.   Filter, wash, ignite and weigh as directed
on p. 258.

3. Direct Determination of Phosphoric Acid as Ammonium Phosphomolyhdate (Finkener)[2]

The precipitate produced as described under 1 is heated until it hecomes changed
to $(NH_4)_3PO_4 \cdot 12MoO_3$. Theoretically this contains 3.784 per cent of P_2O_5, but
better results are obtained if it is assumed to contain 3.753 per cent of P_2O_5 [3]

Baxter[4] recommends heating the precipitate to about 300° as does Ishihashi.[5]
The precipitate then contains 3 784 per cent P_2O_5 and corresponds to the formula
$(NH_4)_3PO_4 \cdot 12MoO_3$. Baxter prepared the molybdate reagent as follows: Dissolve
150 g of commercial ammonium molybdate in 1 l of water and pour into an equal
volume of 6 N nitric acid. Use 50 ml for 0.1 g of P_2O_5. Ishibashi used a 3.5 per
cent solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in pure water. To a neutral solution of
6–70 mg of P_2O_5 he ndded twice the theoretical requirement of molybdate solution,
20 ml of 5 N ammonium nitrate solution, and 20 ml of 5 N nitric acid, making a
total volume of nbout 100 ml. He heated with stirring at 60° for 5 minutes, allowed
to stnnd 3 hours, filtered into n filtering crucible, washed with 2 per cent nitric acid,
heated slowly to 250°, and kept at 250–300° for 30 minutes.

Procedure.   Precipitate the phosphoric acid with ammonium molyb-
date as directed on p. 373; filter the precipitate into a Gooch crucible,
wash with ammonium nitrate solution until very little brown coloration
is produced in the filtrate upon adding $K_4[Fe(CN)_6]$, and dry in a cur-
rent of air at 160° until a constant weight is obtained.   If the pre-
cipitate should become slightly greenish, add a small crystal of
ammonium nitrate and one of ammonium carbonate and again heat
the contents of the crucible, whereupon the precipitate will at once
assume a homogeneous yellow color.

Remark.   The results of Hundeshagen and Steffan show that this method gives
very exact results. Steffan worked precisely according to the directions of Finkener,
precipitating the phosphoric acid in the cold with a 33⅓ per cent solution of nmmo-
nium molyhdate and filtering after standing 24 hours. It is, however, not necessary,
as Hundeshagen has shown, to work with such a concentrated solution of ammonium
molyhdate; the precipitation from a hot solution with a 3 per cent molyhdate solu-
tion yields just as accurate results and the solution does not have to stand so long

[1] See p. 370.

[2] Ber., 11 (1878), 1640.

[3] Hundeshagen, loc. cit.

[4] Am. Chem. J., 28, 298 (1902).

[5] Mem. Coll. Sci., A, 12, 135 (1929).

before filtering. Even when iron is present this method gives good results, so that it is to be recommended for the determination of phosphorus in iron and steel.

4. Determination of Phosphoric Acid as Phosphomolybdic Anhydride (Woy)

Gently ignite the precipitate, produced in the same way as before, until a greenish black residue remains of the composition $24MoO_3 \cdot P_2O_5$, with 3.94 per cent of P_2O_5. Perform the ignition as follows: Upon the bottom of a nickel crucible place a disk of ignited asbestos about 2 mm thick, or the porcelain plate of a Gooch crucible may be used. Upon this place the Gooch crucible containing the precipitate, cover with a watch glass, and heat at first gently and finally until the bottom of the nickel crucible is at a dull red heat. When the precipitate has become of a homogeneous, bluish black color, allow to cool in a desiccator and weigh.

This method is rapid and gives good results in the presence of iron and aluminum.

Determination of Phosphorus in Iron, Steel, and Bronze[1]

Phosphorus is present in all kinds of iron and steel as well as in the various alloys used in steel-making. In general, it is detrimental, and the permissible quantities are usually defined rigidly in specifications of material. Phosphorus is sometimes added intentionally in the manufacture of sheet steel to prevent the sheets from sticking together during the rolling process.

The phosphorus content of most steels lies between 0.01 and 0.1 per cent; ingot iron contains less than 0.01 per cent, and wrought iron usually between 0.1 and 0.2 per cent. In most steels it exists as a solid solution of iron phosphide, Fe_3P, in iron; but in many samples of cast iron, free iron phosphide is found. In wrought iron and in some low-carbon Bessemer steels it is possible that a little phosphate may exist.

The presence of too much phosphorus in steel causes brittleness; the metal is likely to break when subjected to sudden stress.

All methods for determining phosphorus in iron and steel are based upon the preliminary oxidation of the phosphorus to phosphoric acid. Practically all phosphates except those of the alkali metals are insoluble in water, but the phosphoric acid obtained in the chemical examination of iron and steel is usually precipitated first as ammonium phosphomolybdate or as ferric phosphate.

The gravimetric methods are based upon the separation of the phosphoric acid from at least the greater part of the iron by precipitation either as ammonium phosphomolybdate or as ferric phosphate; in the latter case the greater part of the iron is reduced to the ferrous condition after the complete oxidation of the phosphorus and enough is left in the ferric condition so that in carrying out a basic acetate separation all the phosphorus is precipitated as ferric phosphate and the excess ferric iron as basic ferric acetate. From his study of qualitative analysis, the student is already familiar with this method of separating phosphate from bivalent cations.

[1] G. E. F. Lundell, *Ind. Eng. Chem.*, **15**, 171 (1923).

The basic ferric acetate precipitate can be dissolved in dilute hydrochloric acid, and the precipitation of ferric hydroxide or of ferric phosphate by neutralization with ammonia can be prevented by adding considerable citric or tartaric acid. Then on adding " magnesia mixture " to the ammoniacal solution (cf. p. 370) a precipitation of magnesium ammonium phosphate can be obtained. This method of analysis has been recommended but today is seldom used because it is tedious and yields no better results than other, more convenient procedures.

To separate a small quantity of phosphoric acid from a large quantity of iron, it is customary to precipitate the former as ammonium phosphomolybdate by adding ammonium molybdate reagent to the nitric acid solution. The yellow precipitate is least soluble in dilute acids containing considerable dissolved salt. The dry precipitate weighs about 61 times as much as the phosphorus it contains, as is evident from its formula, which is usually written $(NH_4)_3PO_4 \cdot 12MoO_3$. The yellow ammonium phosphomolybdate can be converted into magnesium ammonium phosphate. Even today this method of analysis is applied to the determination of phosphorus in steel in "umpire analyses" to settle disputes among chemists. Many years of experience have shown that the so-called "rapid methods" are just as accurate as the longer methods when properly carried out, but they are sensitive to slight changes in the conditions such as the temperature, time allowed for the completion of the reaction, concentration, and acidity. Rapid methods are sometimes based on the weight or volume of the ammonium molybdate precipitate. Thus the precipitate is sometimes weighed after drying a definite time at a definite temperature and at other times its volume is read after centrifuging in a graduated tube. In Chapters XIV and XV, more convenient, accurate titrimetric methods will be described.

Procedure for Cast Iron. Dissolve 1–3 g of sample in a covered casserole in 30 ml of 7.5 N nitric acid. When all the iron is in solution, add 10 ml of 6 N hydrochloric acid, evaporate to dryness, and bake on the hot plate for 15 minutes. Cool, drench the residue with concentrated hydrochloric acid, dilute to 50 ml, and heat until all the salts are in solution. Filter without delay, wash the residue with 0.6 N hydrochloric acid, and evaporate the filtrate to sirupy consistency. Meanwhile ignite the above residue in a platinum crucible, cool, and heat with 10 drops of concentrated hydrochloric acid and 2 ml of hydrofluoric acid. Evaporate just to dryness, add 5 ml of concentrated hydrochloric acid, and add to the main solution that is being evaporated.

When the solution is of sirupy consistency, transfer to a 300-ml Erlenmeyer flask by alternate rinsing with 7.5 N nitric acid and hot water, using not more than 30 ml of the acid and 70 ml of the water. Heat to boiling and digest for 10 minutes.

Precipitation. To the boiling solution, add 100 ml of acid ammonium molybdate solution (cf. p. 373), shake 10 minutes, and allow to stand at least 4 hours. If an appreciable amount of vanadium is present, carry out the precipitation at 20° in a solution which has just been treated with 2–3 ml of 10 per cent ferrous sulfate solution and a few drops of sulfurous acid to reduce quinquevalent vanadium. Decant off the solution

through a filter, keeping as much of the precipitate as possible back in the flask, and wash with not more than 50 ml of cold 1 per cent nitric acid. Dissolve the precipitate in 24 ml of 6 N ammonium hydroxide to which 2 g of citric acid has been added. Pour the solvent through the filter that contained some of the phosphomolybdate and catch the solution in the flask containing the bulk of the precipitate. Finally wash the filter several times with 0.6 N hydrochloric acid. If the ammoniacal filtrate is not clear, heat it to boiling, filter through the same filter, and wash with hot water. In this case, and whenever appreciable quantities of elements like titanium, zirconium, and tin are present, preserve this filter paper and treat it together with the filter referred to in the following directions.

Make the ammoniacal solution acid with hydrochloric acid, add 20 ml of magnesia mixture, and precipitate magnesium ammonium phosphate as described on p. 373. Allow the precipitate to stand 4 hours. Filter, keeping the precipitate back in the flask as much as possible. Dissolve the precipitate on the filter with 28 ml of 6 N hydrochloric acid, catching the solution in the flask containing the bulk of the precipitate. Wash the filter thoroughly with 0.6 N hydrochloric acid. If titanium, zirconium, or tin is present, ignite this filter, and the one previously set aside, in a platinum crucible, fuse with a little sodium carbonate extract with water, and add the aqueous extract to the hydrochloric acid solution of the first magnesium ammonium phosphate precipitate.

Transfer the solution to a 200-ml beaker. If considerable arsenic is present precipitate with hydrogen sulfide, washing the arsenic sulfide precipitate with dilute hydrochloric acid saturated with hydrogen sulfide. Boil off the excess of hydrogen sulfide and reduce to 50-75 ml. If only a little arsenic is present, add 0.6-1 g of ammonium bromide and evaporate the solution to a volume of 5-10 ml; the arsenic will volatilize as arsenic trichloride.

To the solution free from arsenic, and at a volume 50-75 ml, add 0.1-0.2 g of citric acid and 2-3 ml of magnesia mixture, and again precipitate magnesium ammonium phosphate.

Ignite and weigh the magnesium pyrophosphate as described on p. 258.

Plain Carbon Steel. Dissolve 1-3 g in 50 ml of 6 N nitric acid. When all the steel has dissolved, boil and slowly add a saturated solution of potassium permanganate until oxides of manganese are precipitated. Clear the solution by cautious addition of 10 per cent ferrous sulfate solution, boil gently for 10 minutes, and treat at 70° with 50 ml of ammonium molybdate solution prepared according to Method 2 or 3 on p. 373 and continue as described there.

Alloy Steels. Treat *chromium* steels in the same way, but if any residue is obtained on dissolving in nitric acid, continue heating until it dissolves, adding sulfuric acid if necessary. Treat a high-*silicon* steel like cast iron. If *titanium* or *zirconium* is present to any extent, a phosphate may precipitate during the boiling prescribed for plain carbon steels. Filter off the precipitate, fuse the residue with sodium carbonate, and add the aqueous extract of the melt to the main solution. *Tungsten* steel does not dissolve in nitric acid. Dissolve 1-3 g in a mixture of 20 ml concentrated nitric acid and 60 ml of concentrated hydrochloric acid in a covered casserole. Heat gently and evaporate to dryness. Remove the cover glass and bake till all the acid is expelled. Cool, and add 30 ml of concentrated hydrochloric acid. Heat until all the iron dissolves, dilute to 100 ml, filter, and wash the residue of tungstic acid with N hydrochloric acid. Evaporate the filtrate to a sirup and meanwhile dissolve the tungstic acid in hot $2 N$ ammonium hydroxide, finally washing the paper with dilute hydrochloric acid. Make the ammoniacal solution faintly acid; add 1 g of alum and then add ammonium hydroxide in slight excess. Filter off the aluminum hydroxide and phosphate; dissolve in hot hydrochloric acid and add the solution to the main solution which is being evaporated. Dilute the sirup as described for the analysis of cast iron.

Bronze.

The Lead Molybdate Method

Ibbotson[1] prefers to base the phosphorus determination upon the weight of $PbMoO_4$ that can be obtained from the $(NH_4)_3PO_4.12MoO_3$ precipitate. The $PbMoO_4$ weighs 142 times as much as the phosphorus originally present. For determining small quantities of phosphorus this is one of the quickest and most accurate methods.

Filter the ammonium phosphomolybdate precipitate (see p. 373) and wash it on a 9-cm ashless filter paper with cold 1 per cent nitric acid (1 ml concentrated acid and 100 ml water) at least 10 times. Dissolve the precipitate by pouring 4 ml of concentrated NH_4OH on the filter. Catch the solution in the flask used for the precipitation, wash the paper once with hot water, and again pour this solution through the filter, this time catching it in a 150-ml beaker. Wash the paper at least 6 times with a stream of hot water directed against the upper edge of the paper and then place the solution on a hot plate. Place beside it a 250-ml beaker containing a filtered solution of 10 g NH_4Cl and 12.5 g of ammonium acetate in 50 ml of water. When both solutions are at

[1] *Chemical Analysis of Steel Works' Materials.*

the boiling point, add, to the ammoniacal solution of the yellow precipitate, 10 ml of concentrated hydrochloric acid and 10 ml of 4 per cent lead acetate solution. At once pour this mixture into the hot solution of ammonium chloride and acetate, and wash out the beaker with hot water. Allow the precipitate to settle for a few minutes and then filter through a weighed Gooch crucible. Wash thoroughly with hot water until free from chloride, dry in the hot closet at 105°, and weigh. If preferred, finish the washing with alcohol and ether (cf. p. 258).

In this method of analysis, 12PhMoO₄ are obtained for each P present. The weight of phosphorus, therefore, is found by the formula:

$$\text{wt. ppt.} \times \frac{P}{12PhMoO_4} = \text{wt. ppt.} \times \frac{31.02}{4406} = \text{wt. ppt.} \times 0.00704$$

Determination of Phosphoric Acid in Silicates

In the analysis of silicates (see p. 414) the phosphoric acid is found in the precipitate produced by ammonia in the filtrate from the silica together with iron and aluminum hydroxides. It is analyzed according to p. 171.

Determination of Phosphoric Acid in Mineral Waters

To 5–6 l of the water add a little hydrochloric acid and evaporate to dryness; moisten the residue with concentrated hydrochloric acid, take up with water, and filter off the silicic acid. To the filtrate add a slight excess of ammonia; the phosphoric acid is usually completely thrown down in the form of phosphate of iron, aluminum, or alkaline earth. Dissolve the filtered and washed precipitate in nitric acid, and determine the phosphoric acid according to one of the molybdate methods (pp. 373–379).

Remark. If the mineral water does not contain much iron, aluminum, or alkaline-earth metal, but is rich in phosphoric acid and the alkalies, the precipitate produced by ammonia will not contain all the phosphoric acid. In such a case evaporate the hydrochloric acid solution from the silica several times to dryness with nitric acid, dissolve the residue in as little nitric acid as possible, and determine the phosphoric acid by one of the molybdate methods.

Determination of Phosphorus in Organic Substances

The substance is decomposed by the method of Carius. By the action of the nitric acid in the closed tube the phosphorus is oxidized to phosphoric acid and this is determined as usual.

SEPARATION OF PHOSPHORIC ACID FROM THE METALS

1. Separation from the Metals of Groups I and II

Hydrogen sulfide is conducted into the hydrochloric acid solution,[1] by which means all the members of these groups are precipitated as sulfides while the phosphoric acid remains in solution.

2. Separation from the Metals of Group III

(a) The phosphoric acid is first precipitated as ammonium phosphomolybdate according to p. 373. In order to determine the metals, evaporate the solution containing molybdenum, but free from phosphoric acid, with sulfuric acid to a sirupy consistency, and carefully heat over a free flame until the nitric acid is expelled. After cooling, moisten the residue with hydrochloric acid and take up in water. Place the solution in a pressure flask, saturate with hydrogen sulfide, stopper the flask, and heat for some time on the water bath; the molybdenum is precipitated as flocculent MoS_3. After cooling, slowly open the pressure flask and filter off the molybdenum sulfide. Analyze the filtrate, now free from phosphoric acid and molybdenum, for the metals as described on pp. 148–220.

(b) Separate the phosphoric acid as before, make the filtrate slightly ammoniacal, and saturate with hydrogen sulfide. After standing for some time the solution becomes reddish yellow in color, and the precipitate can then be filtered off. The metals of this group will be found in the precipitate while the molybdenum is in the filtrate in the form of its sulfo salt.

Remark. If nickel is present, some of it will remain in the filtrate with the molybdenum on account of the solubility of nickel sulfide in ammonium sulfide, so that method (a) will then give more accurate results. Vanadium (and tungsten) will also go with the molybdenum.

3. Separation of Phosphoric Acid from Iron, Cobalt, Manganese, and Zinc

If the solution contains iron in the ferric form, acidify with hydrochloric acid, saturate with hydrogen sulfide, and for each gram of the mixed oxides add 3 g of tartaric acid; make the solution slightly ammoniacal and allow to stand over night in a stoppered flask. The precipitate contains the metals as sulfides free from phosphoric acid.

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[1] When silver is present it is precipitated as silver chloride, filtered off, and the filtrate treated with hydrogen sulfide.

Filter, wash with water containing ammonium sulfide, dissolve in acid, and analyze according to pp. 148–220.

4. Separation from Chromic Acid

If the solution contains free alkali or alkali carbonate, make acid with nitric acid, then slightly alkaline with ammonia, and precipitate the phosphoric acid with " magnesia mixture " as described on p. 370.

5. Separation from Calcium, Strontium, Barium, Magnesium, and the Alkalies

Add ammonium carbonate to the hydrochloric acid solution until a slight permanent turbidity[1] is produced, and dissolve this with a few drops of hydrochloric acid. Then add ferric chloride drop by drop until the liquid above the yellowish white precipitate of ferric phosphate becomes distinctly brown in color. Dilute the solution with water to a volume of 300–400 ml, boil for 1 minute, filter, and wash with water containing ammonium acetate. In the filtrate are the alkaline earths and alkalies, which, after expelling the ammonium salts by igniting the residue obtained after evaporating to dryness, are determined in the usual way (see pp. 244–286).

Determination of Phosphoric Anhydride in Apatite

Weigh out duplicate portions of the finely powdered mineral of 0.2–0.25 g, taking care to get the nearest tenth of a milligram as accurately as possible. Heat in a covered 200-ml casserole with 15 ml of 6 N nitric acid. Evaporate to dryness on the steam bath or hot plate, taking care to avoid spattering. Heat the residue for at least 15 minutes at 110–120° to dehydrate silica. Digest the residue with 25 ml of 6 N nitric acid, and heat a few minutes to dissolve the soluble material. Filter and wash with small portions of hot water, receiving the filtrate and washings in a 300-ml Erlenmeyer flask. Continue to wash until 5 ml of the filtrate will give no precipitate of calcium phosphate when neutralized with ammonia. If a precipitate is obtained, pour the test back into the filtrate. The volume of the solution should not exceed 100 ml at this point.

To the filtrate, carefully add 6 N ammonium hydroxide solution until a slight permanent precipitate is produced of calcium phosphate. Dissolve this by adding a few drops of 6 N nitric acid. Heat the solution

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[1] If only alkalies are present there will be no turbidity; add the ammonium carbonate until the solution is neutral.

to about 65°, and add 75 ml of ammonium molybdate reagent.[1] Keep the solution at this temperature for half an hour, filter, and wash once by decantation with an acid solution of ammonium nitrate[2] and at least 6 times on the filter. When the washing is complete place the flask containing the bulk of the precipitate under the funnel and allow 6 N ammonium hydroxide solution to drop upon the upper edge of the filter from a buret, until enough has been added to dissolve all the precipitate on the filter paper and that in the flask. Rotate the contents of the flask from time to time and avoid using an unnecessary excess of ammonia. Wash the filter paper thoroughly with hot water. The volume should not exceed 200 ml at this point. Drop a piece of sensitive litmus paper into the solution and add 6 N hydrochloric acid, with constant rotation of the flask, until the litmus paper in the solution turns pink. Add 10 ml of magnesia mixture and heat almost to the boiling point. Add 2–3 drops of phenolphthalein indicator, and neutralize with 1.5 N ammonium hydroxide until the solution is colored pink by the indicator. Cool, add one-fifth of the solution's volume of concentrated ammonium hydroxide, and allow to stand for at least 4 hours. Continue the analysis by any one of the methods described on p. 258 for treatment of the $MgNH_4PO_4 \cdot 6H_2O$ precipitate in the determination of magnesium.

THIOSULFURIC ACID, $H_2S_2O_3$.   Mol. Wt. 114.14

Form: Barium Sulfate, $BaSO_4$

Treat the aqueous solution of the alkali thiosulfate with an ammoniacal solution of hydrogen peroxide, or with ammoniacal percarbonate solution, heat for some time on the water bath, and then boil to destroy the excess reagent. Make the solution acid with hydrochloric acid, and precipitate the sulfuric acid formed by the above treatment as barium sulfate. Two moles of $BaSO_4$ correspond to 1 mole of $H_2S_2O_3$.

A much better procedure for the estimation of thiosulfuric acid will be discussed under "Iodimetry," Chapter XV.

The remaining acids of this group, arsenious, arsenic, vanadic, and chromic, have been discussed under the respective metals; periodic acid is analyzed in precisely the same way as iodic acid.

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[1] See p. 373 for the composition of the reagent.   If the slightly ammoniacal reagent is preferred, omit the neutralization with NH_4OH.

[2] Mix 100 ml of 6 N ammonium hydroxide with 325 ml of 6 N nitric acid and dilute with 100 ml of water.

CHAPTER X

GROUP V OF ANIONS

NITRIC, CHLORIC, AND PERCHLORIC ACIDS

NITRIC ACID, HNO_3. Mol. Wt. 63.02

Forms: Nitron Nitrate, $C_{20}H_{16}N_4 \cdot HNO_3$; Nitrogen Pentoxide, N_2O_5; Ammonia, NH_3; Nitric Oxide, NO, and Volumetrically

1. Determination of Nitric Acid as Nitron Nitrate[1]

The base diphenylendoanilohydrotriazole, $C_{20}H_{16}N_4$
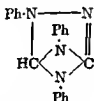
called *nitron* for short, forms a fairly insoluble, crystalline nitrate, $C_{20}H_{16}N_4 \cdot HNO_3$, which can be used for the separation and quantitative estimation of this acid. To prepare the reagent nitron acetate, dissolve 10 g of nitron in 100 ml of 5 per cent acetic acid. It keeps fairly well in a dark bottle.

Procedure. Take a sample equivalent to not more than 0.1 g of nitric acid, and dissolve in 80–100 ml of water containing 1 ml of glacial acetic acid. Heat the solution nearly to boiling and add at one time 10–12 ml of nitron acetate solution. Allow the precipitate to stand 24 hours in a dark place, then filter into a Gooch or Munroe crucible and drain as completely as possible from the pale yellow mother liquor. Wash with 50 ml of ice water saturated with nitron nitrate, added in small portions, and drain the precipitate well after each washing. Dry at 110° for 2 hours. The precipitate contains 16.79 per cent of HNO_3.

Remarks. The method gives good results in the presence of sulfate and iodate ions. If large quantities of chloride are present a correction should be applied, as determined by an analysis with pure nitric acid and the same weight of chloride. In 100 ml of very dilute acid, approximately the following weights of nitron salts dissolve: 0.0099 g of nitrate, 0.008 g of perchlorate, 0.017 g of iodide, 0.04 g of thiocyanate, 0.06 g of chromate, 0.12 g of chlorate, 0.19 g of nitrite, 0.61 g of bromide.

[1] M. Busch, *Ber.*, 38, 861 (1905); A. Gutbier, *Z. angew. Chem.*, 1905, 491.

The results of the nitric acid determination are a little high rather than low, owing to occlusion of a little precipitant.

Besides the acids represented by the above difficultly soluble salts, ferro- and ferricyanic, picric, and oxalic acids interfere with the determination. Hydrobromic acid can be decomposed by adding chlorine water, drop by drop, to the boiling solution until the yellow color of bromine disappears, hydriodic acid by adding an excess of potassium iodate to the neutral solution and boiling off the iodine. Nitrous acid can be removed by dropping powdered hydrazine sulfate into the concentrated solution and chromic acid by reduction with hydrazine sulfate.

2. Determination of Nitric Acid as Nitrogen Pentoxide[1]

This method is based upon the fact that, when an intimate mixture of a dry nitrate is heated with an excess of silica, nitrogen pentoxide is evolved and the amount is determined by the loss in weight:

$$2NaNO_3 + SiO_2 = Na_2SiO_3 + N_2O_5$$
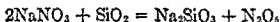
This method cannot be used when any other volatile substance is present, which is usually the case.

3. Determination of Nitric Acid as Ammonia[2]

The usual method for the determination of nitric acid is to reduce it in alkaline solution to ammonia by means of aluminum, zinc, or, best, Devarda's alloy (cf. Vol. I):

$$NO_3^- + 4Zn + 7OH^- \rightarrow 4ZnO_2^= + NH_3 \uparrow + 2H_2O$$
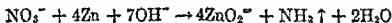
After the reduction, the solution is distilled into a known quantity of acid and the excess of the acid found by titration, or the ammonia can be determined as ammonium chloroplatinate or as platinum (cf. pp. 287–288, *b* and *c*).

Procedure. Place about 0.5 g of the nitrate in a 500-ml Erlenmeyer flask (Fig. 64) and dissolve in 110 ml of water. To this solution add 5 ml of alcohol, 50 ml of caustic potash (*d* 1.3), and 2–2.5 g of powdered Devarda's alloy. Or, instead of Devarda's alloy, use 5 g of well-washed zinc and 2 g of ferrous sulfate. For the caustic potash solution, 80 ml of saturated sodium hydroxide solution can be substituted. At once connect the flask with the distillation apparatus shown in the figure. The left arm of the 250-ml Péligot tube, *A*, is connected by a curved tube with the middle bulb, so that a spurting back of the liquid is avoided. The delivery tube (of potash glass) connecting the flask *K* with the tube *A* is about 1 cm in diameter and is provided with a small opening

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[1] Reich, *Z. Chem.*, **1**, 86 (1862).

[2] Devarda, *Z. anal. Chem.*, **33**, 113 (1894); Pannertz, *Z. anal. Chem.*, **39**, 318 (1900).

at o, inside the flask, to prevent spurting of condensed liquid over into
A. Place exactly 20.00 ml of 0.5 N sulfuric acid in A and dilute so that
the solution just reaches to each of the bulbs on the side. Place exactly
5.00 ml of the acid in B, with a few drops of methyl orange indicator
solution, and dilute in the same way. Connect the tubes A and B by
means of a T-tube, of which the upper end is closed by a pinchcock upon
a piece of rubber tubing, so that a piece of red litmus paper may be intro-
duced here if it is desired to see whether NH₃ is escaping.

When all is ready, gently heat the contents of the flask K to start
the reaction, then remove the flame and allow the reaction to proceed
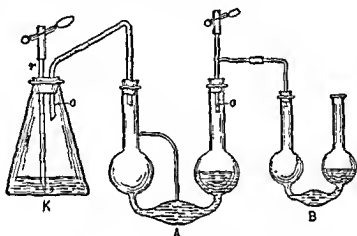
FIG. 64.

by itself. After an hour this will be shown to be complete by the
cessation of the hydrogen evolution. Then slowly heat the liquid in K
to boiling, and keep at this temperature until about half of the liquid
has distilled over into A; this requires about half an hour. During
the last 10 minutes pass a slow current of air through the tube r.

If the distillation has been correctly performed, all the ammonia
will now be found in A; no trace should reach B, and the red litmus
paper in the T-tube should show no tinge of blue.

When the distillation is finished, open the pinchcock at r and remove
the flame. Add a little methyl orange to A whereby the liquid is
colored red, pour the contents of B into A and rinse out B with water
that is added to A. Finally titrate the excess of the sulfuric acid with
0.5 N caustic alkali solution until a yellow end point is obtained. The
amount of nitric acid is computed as follows:

If t ml of 0.5 N base is used in the titration of a g of substance, then

$$\frac{(25 - t) \times 3.151}{a} = \text{per cent HNO}_3 \text{ or } \frac{(25 - t) \times 2.700}{a} = \text{per cent N}_2O_5.$$

Determination of Nitric Acid as Nitric Oxide

Method of Schlösing and Grandeau, modified by Tiemann and Schulze[1]

Principle. If a nitrate is heated with ferrous chloride and hydrochloric acid, the nitric acid is reduced to nitric oxide:

$$NaNO_3 + 3FeCl_2 + 4HCl = NaCl + 3FeCl_3 + 2H_2O + NO$$
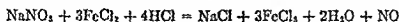
From the volume of the nitric oxide its weight can be calculated.

The method of Schlösing in its original form[2] was not much used on account of the apparatus required; but after being modified by Grandeau[3] it became one of the best methods for the determination of nitric acid.

The apparatus necessary, shown in Fig. 65, consists of a 150-ml flask K fitted with a double-bored rubber stopper. Through one of the holes pass the tube b, which
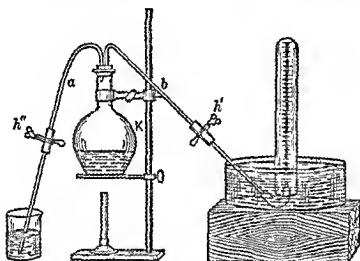
Fig. 65.

reaches into the flask just to the lower surface of the stopper; through the other hole pass the tube a,[4] ending in a restriction about 1 mm wide and reaching 1½ cm below the stopper. Connect the tube b by means of a piece of rubber tubing 5 cm long, and provided with a pinchcock, with a second tube whose lower end reaches up into the measuring tube and is covered with rubber tubing as is shown in the figure. In the same way connect the tube a with a straight tube.

Solutions Required. 1. A nitrate solution of known strength; dissolve 2.022 g of recrystallized potassium nitrate, dried at 160°, in 1 l of water. At 0° and 760 mm pressure, 50 ml of this solution evolves 22.39 ml of NO.

2. Ferrous chloride solution. Dissolve 20 g of iron (nails) in 100 ml of concentrated hydrochloric acid

3. Six normal hydrochloric acid d 1.1.

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[1] *Z. anal. Chem.*, **9**, 401 (1870), and *Ber.*, **6**, 1041 (1873).

[2] *Ann. chim. phys.*, [3] **40**, 479 (1853).

[3] Grandeau, *Analyse chimique appliquée à l'agriculture.*

[4] Grandeau used a separatory funnel instead of the tube a; the latter was proposed by Tiemann and Schulze.

Procedure. Pour 10 ml of water into K and mark its upper level on the outside of the flask with a colored pencil, then add 40 ml more and mark its position.

Now pour out the water and add from a pipet exactly 50.00 ml of the standard nitrate solution to K, insert the stopper with the delivery tubing in place, and open the pinchcocks h' and h''. Heat the contents of the flask to boiling with a free flame until no more bubbles of air escape from the lower end of b into the bath containing boiled water. To make sure that all the air is expelled from the apparatus, pinch the rubber tubing at h' with the thumb and finger; if no air is present, the liquid will quickly rise in b, exerting a noticeable pressure. Then close the pinchcock h' and continue the boiling until the 50 ml has been reduced to a volume of 10 ml; then remove the flame and close the pinchcock h''. The lower end of a, which dips into distilled water, is immediately filled up to the pinchcock. The vapors in the flask condense, forming a vacuum, as shown by the closing together of the rubber tubing at h' and h''.

Pour 30 ml of the ferrous chloride solution into a beaker and mark the upper level on the outside with a colored pencil; add 20 ml more and note its position in the beaker again. Place the lower end of the tube a in the ferrous chloride solution so that it reaches below the lower mark on the beaker, and, by opening h'', allow 20 ml of the solution to pass into the flask K. Then replace the beaker containing the ferrous chloride with one containing boiled water. The tube a should not extend vertically into the water, but should be inclined as much as possible. The specifically heavier ferrous chloride solution in the tube passes into the water, and the water takes its place. When the lower end of a has become filled with pure water in this way, dip it into a beaker containing 6 N hydrochloric acid and allow about 20 ml of the acid to flow into K, and finally add 3–4 ml of water to replace the acid in a. Now fill a 50-ml measuring cylinder with boiled water, place over the lower end of b as shown in the figure, and heat the contents of the flask K 15 minutes on the water bath,[1] then boil with a free flame. As soon as the compressed rubber tubing begins to expand open h', but at the same time pinch the rubber tubing between the thumb and finger. When the liquid no longer rises in b, remove the hand from the rubber tubing and allow the nitric oxide to collect slowly in the measuring tube. After half of the liquid has evaporated, no further evolution of nitric oxide is to be noticed, although the brown color of the solution shows that the gas has not been completely expelled.

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[1] The heating on the water bath is necessary, as otherwise a little nitric acid will distil over and not be reduced. A. Wegelin, Inaug. Dissert., Zurich, 1907.

To accomplish this, remove the flame, close h', and allow the liquid in K to cool. By means of the vacuum thus produced the remainder of the nitric oxide is expelled from the solution. Repeat the boiling once more, with the same precautions, until the lower mark is reached. Remove the flame, close h', and place the measuring tube containing the nitric oxide in a cylinder containing pure water at the temperature of the room. To prevent the tube containing the gas from sinking, encase its upper end in a large cork so that it floats on the water. After allowing to stand for 15–20 minutes raise the tube, by means of the cork, until the level of the liquid within stands at the same height as that in the cylinder without, and read the volume of the gas. At the same time take the temperature of the water and note the barometer reading.

If the temperature was $t°$, the barometer reading B ml, and w the tension of aqueous vapor at $t°$, then the corresponding volume at $0°$ and 760 mm pressure is

$$V_0 = \frac{V(B - w)273}{760(273 + t)}$$

Now 50 ml of the standard potassium nitrate solution contains 0.1011 g of KNO_3 corresponding to 0.05401 g of N_2O_5, so that the volume V_0 of the nitric oxide corresponds to 0.05401 g of N_2O_5. Repeat the experiment several times and use the mean value. It is not permissible to assume that 0.1011 g of KNO_3 will furnish exactly 22.39 ml of nitric oxide as a little always remains in the flask.

Now carry out the same procedure with 50 ml of the solution of the unknown nitrate, which should be prepared so that the amount of nitric oxide evolved will be about the same as that from 50 ml of the standard solution.

Good results are obtained by this method, but the rubber stoppers are attacked quite badly and analyses are sometimes spoiled by not opening the pinchcock h' at just the right time. These difficulties have been overcome by Wegelin[1] in the apparatus shown in Fig. 66. The decomposition flask K has a capacity of about 120 ml. Its neck is about 9 cm long, and into it are fused glass tubes k and s connecting the flask with the funnel T and the delivery tubing G. The results are a little too high by this method so that it is advisable to carry out the standardization with about the same quantity of nitrate as taken for actual analysis.

Modified Procedure. Through the funnel T pour the concentrated solution of the weighed nitrate and rinse out the funnel with 50 ml

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[1] Doctorate Thesis, Zürich, 1907.

of water. Close the stopcock a, and boil the liquid in K. Have the 75-cm-long tube g in place, dipping under mercury in the small dish G, but do not have the tube C over the end of the tubing. After half the liquid in K has boiled away, remove the flame and allow mercury to suck up into the tube g. Mark the height of the mercury; if it does not fall during 15 minutes, the apparatus is tight. Again heat the liquid in K to boiling, and when steam escapes, at the bottom of g, open the stopcock Q_1 and drive out all air from the tubing k. Boil, with Q_1 open, until the liquid in K is reduced to 10 ml as shown by the mark etched on the flask. Then close Q_1 and allow the liquid in K to
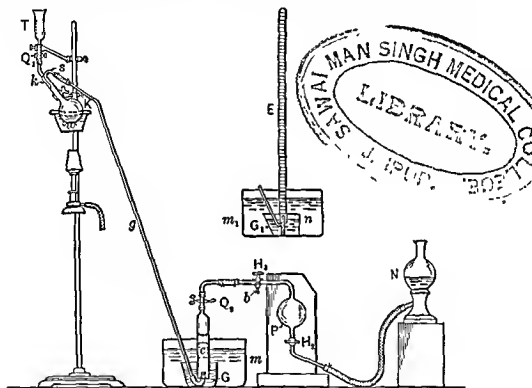
FIG. 66.

cool a little. Pour 20 ml of standard ferrous chloride solution into T and cause it to flow into K by carefully opening the stopcock but taking care not to let any air in. Rinse out T with 80 ml of 6 N hydrochloric acid and place the cylinder C, filled with mercury, over the end of the tubing g. Heat the contents of K 20 minutes, with the water bath W in place, and then boil with a free flame until the volume of liquid is reduced to 10 ml. Remove the flame and transfer the gas in C into the Drehschmidt pipet, P, by lowering the leveling bulb N, and opening H_1 and Q_2. Also introduce 0.5 ml of 33 per cent caustic potash solution through the tip of the stopcock H_1. This serves to

absorb hydrochloric acid gas. After a little while, transfer the gas to a gas buret and measure it over mercury or over water.

It is also permissible to collect the gas over water. In that case have the 75-cm tube g end in a 6–7 cm T-tube G_1 open at both ends. Fill the dish n with mercury till level with the upper end of the T-tube, and place n in the dish m_1 containing water.

Determination of Nitric Acid in a Drinking Water

Evaporate 100–300 ml of the water to 40–50 ml in a porcelain dish, add a few drops of methyl orange indicator solution, and dilute hydrochloric acid, free from nitrate, until the solution is pink. Now add sodium carbonate solution until the liquid is barely alkaline and wash the contents of the flask into the decomposition flask K, Fig. 65, and analyze as described on p. 387, but collect the gas over 10 per cent sodium hydroxide solution, to make sure that the carbonic acid is completely absorbed.

After the experiment with the water to be analyzed, repeat with an amount of the standard solution sufficient to evolve about the same quantity of nitric oxide.

Remark. In drinking water the neutralization of the evaporated sample is not absolutely necessary, except with alkaline mineral waters; in that case the introduction of the hydrochloric acid would otherwise cause such a violent evolution of carbon dioxide that the flask might crack.

CHLORIC ACID, $HClO_3 \cdot 7H_2O$. Mol. Wt. 210.58

Form: Silver Chloride, AgCl, besides volumetric and gasometric methods

To determine chloric acid as silver chloride it must previously be reduced to chloride by means of ferrous sulfate or zinc.

Reduction by Means of Ferrous Sulfate

Dissolve 0.3 g of chlorate in 100 ml of water, add 50 ml of a 10 per cent solution of crystallized ferrous sulfate, heat with constant stirring till the solution begins to boil, and keep at this temperature for 15 minutes. After cooling, add nitric acid until the deposited basic ferric salt is dissolved, precipitate the chloride by means of silver nitrate, and weigh after the usual treatment.

One gram of silver chloride corresponds to 0.8550 g $KClO_3$.

Reduction by Zinc

Although chlorates are reduced in neutral solution by means of zinc or Devarda's alloy, it is not advisable to effect the reduction in this way for quantitative purposes. The same end is reached more expeditiously by adding zinc dust to an acetic acid solution. Treat the dilute chlorate solution with acetic acid until it reacts distinctly acid, add an excess of powdered zinc, and boil the solution for 1 hour. After cooling, add nitric acid in sufficient quantity to dissolve all the excess of zinc, filter if necessary, and determine the chloride as silver salt (p. 291).

Remark. Both the above methods afford exact results, but the former is to be preferred, for it requires less time.

Chlorates are not decomposed quantitatively into chlorides by ignition in open vessels or in a current of carbon dioxide. Some chlorine and a little alkali are always lost, so that, even when the residue is evaporated with hydrochloric acid, too low results are obtained.

According to the two following methods, the decomposition of alkali chlorate into chloride is quantitative.

Reduction with Hydrochloric Acid

Cover 0.3 g of chlorate in a weighed porcelain crucible with $1.5\,N$ hydrochloric acid. Place a watch glass upon the crucible, and heat the contents on the water bath until the evolution of chlorine ceases. Rinse off the lower surface of the watch glass, and evaporate the contents of the crucible to dryness on the water bath. Replace the cover and gently ignite over a free flame until the decrepitation ceases. After cooling in a desiccator, again weigh the crucible.

Reduction by Ignition with Ammonium Chloride

Mix the alkali chlorate in a porcelain crucible with 3 times as much pure ammonium chloride, cover with a watch glass, heat over a free flame, keep in constant motion until the ammonium chloride is completely removed, and weigh the residual alkali chloride.

PERCHLORIC ACID, HClO₄.   Mol. Wt. 100.46

Form: Silver Chloride, AgCl

Perchlorates cannot be reduced to chlorides by means of ferrous sulfate, zinc, or by repeated evaporation with concentrated hydrochloric

acid.[1] On ignition, some chlorine and alkali chloride and probably a little perchloric acid are lost, so that an error amounting to as much as 1 per cent may be expected. On the other hand, Winteler has shown that perchlorates may be changed to chlorides by heating with concentrated nitric acid and silver nitrate in a closed tube (see Carius' method for determining chlorine in organic substances, p. 293), and L. Blangey found that ignition with ammonium chloride would accomplish the same result. With 0.3 g of perchlorate and 2 g of ammonium chloride, 90 minutes should be sufficient for complete reduction.

Decomposition of Perchlorates by Ignition with Ammonium Chloride

By twice igniting an intimate mixture of 0.5 g potassium perchlorate with 1.5–2 g of ammonium chloride in a *platinum* crucible covered with a watch glass, the perchlorate is completely changed to chloride. Care should be taken not to melt the residual chloride, for then the platinum is attacked, although the accuracy of the results is not affected. The reduction cannot be accomplished completely in a porcelain crucible unless platinum is present as catalyzer. If 0.5 g of alkali perchlorate is mixed with 1 g of ammonium chloride, and 1 ml of chloroplatinic acid solution (0.0918 g Pt) is added, a complete reduction can be accomplished by igniting and repeating with 2 more additions of ammonium chloride.

Determination of Perchloric Acid in the Presence of Chloric Acid

In one portion reduce the chlorate, as described on p. 390, with ferrous sulfate, and determine the chloride formed as silver chloride. Ignite a second portion in an old platinum crucible (or in one of porcelain with the addition of 1 ml of chloroplatinic acid) and 3 times as much ammonium chloride (as described above). In this way the total amount of chlorine is obtained, and from these data the amount of each acid can be calculated.

Determination of Perchloric, Chloric, and Hydrochloric Acids in the Presence of One Another

The three acids are assumed to be present in the form of their alkali salts.
In one portion determine the chloride-chlorine by precipitation with silver nitrate. In a second sample determine the chlorate and chloride-chlorine after the chlorate has been reduced to chloride by means of ferrous sulfate. Determine the total amount of chlorine present in a third portion after ignition with ammonium chloride.

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[1] On evaporating with hydrochloric acid there is a loss without any evolution of chlorine; it is due to the volatilization of small amounts of perchloric acid.

CHAPTER XI

GROUP VI OF ANIONS

SULFURIC, HYDROFLUORIC, AND FLUOSILICIC ACIDS

SULFURIC ACID, H_2SO_4. Mol. Wt. 98.08

Form: Barium Sulfate, $BaSO_4$

Theoretically the gravimetric determination of sulfuric acid is extremely simple, it being only necessary to precipitate with barium chloride, filter, and weigh the barium sulfate. Practically, however, it is a process connected with many difficulties.

According to the manner of precipitating barium sulfate, the composition of the precipitate varies in such a way that sometimes the results are too high and sometimes too low.

Errors Which May Occur in the Precipitation of Barium Sulfate. *I. In the Precipitation of Barium Chloride with Pure Sulfuric Acid.* If a dilute, slightly acid solution of barium chloride is treated at the boiling temperature with an excess of dilute sulfuric acid, the precipitate contains all the barium except a very small, negligible amount. If, however, the precipitate is weighed, the result is invariably too low; and this is true even when the solution is evaporated to dryness in order to recover the last traces of barium. The precipitate always contains barium chloride in a form which cannot be removed by washing. A mixture, therefore, of barium sulfate and barium chloride is weighed, and as the molecular weight of the chloride is less than that of the sulfate, the result must be too low. To obtain accurate results, the chlorine combined with barium in the precipitate must be replaced by SO_4; and this can be accomplished by moistening the precipitate with concentrated sulfuric acid, and heating until the excess of the acid is removed by volatilization.

Not only is barium *chloride* carried down with barium sulfate, but all barium salts as well, especially the chlorate and nitrate. These are, however, readily changed to sulfate by the above treatment with concentrated sulfuric acid. It is immaterial in the estimation of barium how the precipitation is effected; whether the sulfuric acid is added quickly, or drop by drop, the results are always the same.

II. In the Precipitation of Pure Sulfuric Acid with Barium Chloride. This is the reverse process, but here it is not a matter of indifference whether the barium chloride is added slowly, drop by drop, or rapidly all at one time. In the first instance, the results are very near the truth without the application of any correction; in the second, too high results are obtained, because by the rapid addition of the reagent more barium chloride is carried down with the precipitate than when the reagent is added very slowly.

To obtain the true weight of barium sulfate, it is often necessary to make a deduction for the amount of barium chloride contained in the precipitate and to add the weight of barium sulfate remaining in solution.

The chlorine contained in the precipitate can be determined in several different ways.

1. Fuse the precipitate with 4 times as much pure sodium carbonate, extract the melt with hot water, filter, make the filtrate acid with nitric acid, and precipitate the chlorine with silver nitrate. Filter and weigh.

2. Still more accurate is the process of Hulett and Duschak.[1] Place the ignited precipitate of barium sulfate in a U-tube of which one arm is drawn out into a thin, right-angled, gas delivery tube. Add concentrated sulfuric acid to the precipitate and heat the mixture by placing the U-tube in hot water. The barium sulfate dissolves readily in the hot, concentrated sulfuric acid, and the barium chloride present is decomposed. To determine the amount of hydrochloric acid set free, pass a slow stream of air, which has been washed with caustic potash solution, through the tube, with the drawn-out end of the tube dipping into a stout test tube containing 0.01 N silver nitrate solution. After 2–2.5 hours all the hydrochloric acid will have been expelled from the sulfuric acid.

Remove the decomposition apparatus, rinse out the gas delivery tube with a little water, and determine the silver remaining in solution volumetrically (cf. Volhard method).

For the determination of the dissolved barium sulfate, evaporate to dryness the filtrate from the first precipitation, moisten the residue with a few drops of concentrated hydrochloric acid, take up with water, filter off the slight precipitate of barium sulfate, and weigh. During all such work take care to prevent sulfuric acid contamination from the air in the laboratory. The evaporation should, therefore, take place on the steam bath or steam table.

Calculation of the True Weight of Barium Sulfate. If the weight of the first precipitate of crude barium sulfate is a, the weight of the barium chloride contained in this precipitate, as determined by titration of the amount of chlorine, is b, and the amount of barium sulfate in solution is c, then $a - b + c$ represents the weight of pure barium sulfate.

Experience has shown, however, that, when pure sulfuric acid is precipitated by means of dilute barium chloride solution added drop by drop, the errors b and c are approximately equal and counterbalance each other so that the weight a is very close to that of the pure barium sulfate.

III. In the Precipitation of Sulfates with Barium Chloride. Here the relations are far more complicated than in the precipitation of pure sulfuric acid, partly because the barium sulfate is more soluble in salt solutions than in water containing a little acid, and partly because of the tendency of barium sulfate to occlude not only barium chloride but many other salts as well. Solutions of chromium sulfate are either violet or green. From the boiling-hot green solution only one-third of the sulfuric acid is precipitated, the remainder probably being present in the form of a complex chrome-sulfate cation;[2] on cooling, the green solution gradually becomes violet, and after some time all the sulfuric acid is precipitated. The precipitation of barium sulfate in the presence of ferric iron has been much studied. In the boiling-hot solution, not all the sulfuric acid is precipitated and considerable iron is thrown down with the barium sulfate, and furthermore, the precipitate then loses SO_3 on

[1] *Z. anorg. Chem.*, 40, 196 (1904).
[2] Recoura, *Compt. rend.*, 113, 857; 114, 477.

ignition. Since ferric oxide weighs less than an equivalent weight of barium sulfate sometimes the results are as much as 10 per cent too low. On the other hand, Küster and Thiel[1] were able to get satisfactory results (1) by precipitating the sulfuric acid from such a solution in the cold, (2) by slowly adding the ferric chloride and sulfuric acid solution to the hot solution of barium chloride, or (3) by precipitating the iron by an excess of ammonia, heating, adding barium chloride to the solution without filtering off the ferric hydroxide, and finally dissolving the ferric hydroxide in dilute hydrochloric acid.

Most chemists, however, deem it advisable to remove trivalent metals before attempting to determine the sulfuric acid. This is accomplished in the case of ferric iron by adding a liberal excess of ammonia to the dilute, slightly acid solution which is at a temperature of about 70°. If 5–7 ml of concentrated ammonia (d 0.90) is added in excess of the amount required for neutralization,[2] the precipitate is not likely to contain any basic ferric sulfate. If, on the other hand, the solution is barely neutralized with ammonia, the precipitate will invariably contain some sulfate.

The bivalent metals are occluded to a much less extent, so that it is not, as a rule, necessary to remove them. On the other hand, in the presence of considerable amounts of bivalent metal with relatively small amounts of sulfuric acid, the error arising from occlusion is likely to be large, so that it is better to remove the bivalent metals. The error caused by ferric salts can be largely overcome by reducing the iron with zinc.

In the presence of alkali nitrate or chlorate the barium sulfate precipitate will contain considerable quantities of barium chlorate and nitrate which it is impossible to remove by washing with hot water. These acids, therefore, must be decomposed by evaporation with hydrochloric acid before the precipitation of the sulfuric acid is attempted.

In ordinary chemical practice it is usually a question of determining sulfuric acid in a solution containing considerable amounts of ammonium or alkali chloride, ammonium or alkali sulfate, and some free hydrochloric acid. Now ammonium and alkali sulfates are also occluded by barium sulfate, and the amount of occlusion increases as the solution is more concentrated with respect to these substances. For this reason it is evident that barium sulfate should always be precipitated in a dilute solution. On the other hand, if the solution is too dilute or very concentrated the crystals are so small that they will run through a filter. A small amount of free hydrochloric acid is indispensable, but larger amounts have a solvent effect upon the precipitate. One might think that adsorbed ammonium chloride would do no harm, but it has been found to cause some volatilization of sulfate during ignition.

For an amount of sulfuric acid corresponding to 1–2 g of barium sulfate, the precipitation should take place in a volume of 350–400 ml and in the presence of 1 ml of 12 N hydrochloric acid.

If a neutral solution is at hand, dilute to a volume of 350 ml and add 1 ml of concentrated hydrochloric acid. Carefully neutralize an alkaline solution with hydrochloric acid, using methyl orange as indicator, add 1 ml of concentrated hydrochloric acid in excess, and dilute the solution to 350 ml.

Finally, in the case of an acid solution, either evaporate to dryness, moisten the residue with 1 ml of concentrated hydrochloric acid, and add 350 ml of water, or,

[1] Z anorg Chem, 22, 421.
[2] Pattinson, J Soc. Chem. Ind, 24, 7.

with methyl orange as indicator, neutralize the solution with ammonia, add 1 ml of concentrated hydrochloric acid, and dilute to 350 ml.

Remarks. In the presence of ammonium salts the precipitation of the barium sulfate should not be accomplished by the slow addition of the barium chloride, as is otherwise desirable, for, as Hintz and Weber have shown, this leads to low results, whereas the occlusion caused by the rapid addition of the barium chloride counterbalances this error.

Under no circumstances should a precipitate of barium sulfate be heated over a blast lamp, for then sulfuric anhydride is evolved from the barium sulfate.

To explain the occlusion of barium chloride by barium sulfate, Hulett and Duschak[1] suggested that perhaps the precipitate might contain salts such as BaCl·HSO₄, (BaCl)₂SO₄, and Ba(HSO₄)₂, and Folin[2] believed that this was so because some of his precipitates lost SO₃ on ignition while others lost HCl. He also suggested the possibility of salts such as Ba(KSO₄)₂ being precipitated.

Determination of Sulfuric Acid in Insoluble Sulfates

Calcium and strontium sulfates can be decomposed by long digestion with ammonium carbonate solution. Barium sulfate is decomposed so slowly by boiling with a soluble carbonate that it is best to mix with 4 times as much sodium carbonate, fuse in a platinum crucible, extract the melt with water, and wash the barium carbonate residue with sodium carbonate solution. Make the filtrate acid with hydrochloric acid, boil off the carbon dioxide, and precipitate the sulfuric acid as usual.

Lead sulfate can be decomposed by boiling with sodium carbonate solution; after cooling, saturate the solution with carbon dioxide and filter. The lead remains behind as carbonate; the filtrate contains all the sulfuric acid.

For the determination of sulfuric acid in silicates, fuse the finely powdered substance with 6 times as much sodium carbonate, extract the melt with water, make the filtrate acid with hydrochloric acid, and evaporate to dryness to dehydrate the silica. Moisten the residue with a little concentrated hydrochloric acid, take up in hot water, and filter off the silicic acid. Determine the sulfuric acid in this filtrate.

Determination of Sulfuric Acid in the Presence of Soluble Sulfides

Place the substance in a flask, replace the air by carbon dioxide, add dilute hydrochloric acid, and boil the solution while passing carbon dioxide through it until all the sulfide has been expelled. Then precipitate the sulfuric acid from the solution.

[1] Loc. cit.

[2] J. Biol. Chem., 1, 131 (1905).

This determination is used in the analysis of cements but the hydrochloric acid solution of the cement will contain much calcium as well as iron and aluminum. It is best to precipitate these metals by the addition of ammonia and ammonium carbonate and determine the sulfuric acid in the filtrate.

If it is desired to determine the amount of sulfide-sulfur, cover the substance with concentrated hydrochloric acid that is saturated with liquid bromine, dilute, add hydrochloric acid, and boil the solution to expel the excess of the bromine. Precipitate the iron, aluminum, and calcium by ammonia and ammonium carbonate, and determine the total sulfur in the filtrate. The difference between the two results represents the amount of sulfur present as sulfide. For the volumetric determination of sulfuric acid see Chapter XVII.

HYDROFLUORIC ACID, HF. Mol. Wt. 20.01

Forms: Calcium Fluoride, CaF_2; Silicon Fluoride, SiF_4; besides volumetric and gasometric methods

1. Determination as Calcium Fluoride

If the solution contains free hydrofluoric acid or an acid fluoride, add sodium carbonate until the reaction is alkaline and from one-fourth to one-fifth as much more in excess. By the excess of sodium carbonate the subsequent precipitate of calcium fluoride will contain calcium carbonate, which renders the precipitate easy to filter. A pure precipitate of calcium fluoride is slimy, and the pores of the filter become so clogged that it is almost impossible to complete the filtration. To solutions of neutral fluorides, add about 1 ml of a $2 N$ sodium carbonate solution. Heat the alkaline solution to boiling, add an excess of calcium chloride solution, filter, and thoroughly wash the precipitate of calcium fluoride and carbonate with hot water. Dry the precipitate, transfer as much of it as possible to a platinum crucible, add the ash of the filter, and ignite the contents of the crucible. The ignition makes the CaF_2 denser and hence easier to filter. After cooling, cover the mass with an excess of dilute acetic acid; this changes the lime to the soluble acetate, but does not affect the fluoride. Evaporate the mixture to dryness on the water bath; moisten the residue with water and a few drops of $6 N$ acetic acid. Filter off the insoluble calcium fluoride, wash, and dry. Transfer as much of the dried CaF_2 to the crucible as possible, burn the filter paper, add its ash, and after ignition weigh the crucible. To confirm the result treat the substance with a little concentrated sulfuric acid (added cautiously), evaporate off the excess of

the acid, once more ignite, and weigh the contents of the crucible as calcium sulfate. Calcium fluoride is not volatilized in an open platinum crucible heated over a Bunsen burner. Heated over the blast lamp, there is appreciable volatilization.

One gram CaF_2 yields 1.744 g $CaSO_4$.

Remark. The results are usually a little low on account of the solubility of calcium fluoride; 100 ml of water dissolves 0.0016 g and 100 ml of 1.5 N acetic acid dissolves 0.011 g CaF_2 at the temperature of the water bath.

Example: Determination of Fluorine in Calcium Fluoride. Calcium fluoride alone is not decomposed completely by fusing with sodium carbonate; but if mixed with $2\frac{1}{2}$ times as much silica and then fused with 6 times as much sodium-potassium carbonate, the greater part of the silicic acid and all the fluorine will be changed to soluble alkali salts, while the calcium will be left as insoluble calcium carbonate. The mixture must be heated gradually (best in a platinum dish), as otherwise the evolution of carbon dioxide may cause the melt to boil over. The thin liquid fusion soon changes to a thick paste or only sinters somewhat. On raising the temperature, it is almost impossible to melt this mass further, and it is not necessary. In fact, too high a temperature is to be avoided on account of the danger of losing some alkali fluoride by volatilization. The reaction is complete when there is no further evolution of carbon dioxide. After cooling, treat the melt with water, filter off the insoluble residue, and wash thoroughly with hot water. Remove silicic acid by adding 4 g of ammonium carbonate,[1] heat for some time at about 40°, allow to stand over night, and in the morning filter off the voluminous precipitate. Wash it with 2 per cent ammonium carbonate solution (pure water will give a turbid filtrate). The filtrate now contains only a small amount of silicic acid. Evaporate almost to dryness on the water bath,[2] dilute with a little water, and add a few drops of phenolphthalein indicator solution. The liquid is colored pink by the indicator; add enough nitric acid to make it colorless. Heat the solution to boiling, which causes the reappearance of the pink color. After cooling, again discharge the color with nitric acid, and repeat this operation until finally the addition of $1-1\frac{1}{2}$ ml of 2 N nitric acid is sufficient to effect the decolorization.

The solution still contains a little silicic acid which can be removed, as recommended by Berzelius, by precipitating with 2 ml of ammoniacal zinc oxide. To prepare this, add sodium carbonate to a neutral zinc solution, heat to boiling, filter, and wash with hot water. Dissolve the precipitate in the Schaffgottsche ammonium carbonate reagent (p. 289). After the addition of the ammoniacal zinc solution heat to boiling till the ammonia is wholly expelled, filter, and wash the precipitate with hot water.

The above-prescribed use of nitric acid instead of hydrochloric acid is necessary because some phosphate is likely to be present which must be removed. To the still alkaline solution, add silver nitrate in slight excess. This serves to precipitate the phosphate (chromate), chloride, and carbonate of silver. Heat slightly, filter,

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[1] Before adding the ammonium carbonate, the greater part of the alkali carbonate should be neutralized with dilute hydrochloric acid, but care should be taken not to make the solution acid.

[2] The liquid foams during the evaporation owing to the decomposition of the excess of ammonium carbonate; the evaporating dish should be covered with a watch glass until the evolution of carbon dioxide ceases.

and wash with hot water. Remove the excess silver by adding a little sodium chloride solution. Boil to coagulate, filter, and wash the precipitate with hot water. Add 1 ml of 2 N sodium carbonate solution and precipitate with calcium chloride as described on p. 397.

Determination of Silica and Fluorine in Glasses and Enamels

The method just described is tedious. Hoffman and Lundell[1] have modified the procedure, so that the determination of fluorine and silica can be made in silicates in much less time and with greater accuracy. Instead of precipitating the fluorine as calcium fluoride, it is obtained as lead chlorofluoride, PbClF, which can be dissolved in dilute nitric acid and the chloride content determined by titration with silver nitrate (see Chapter XVII, "Volhard Method").

The precipitation of lead chlorofluoride should take place in a solution of pH 3.5–5.6. The presence of as little as 0.5 mg of aluminum causes low results as does more than 50 mg of boron, 0.5 g of ammonium, or 10 g of sodium or potassium. In the volumetric procedure small quantities of silica, phosphates, or sulfates do no harm. Phosphate may cause the filtrate from the lead chlorofluoride precipitate to become turbid.

Lead chlorofluoride is appreciably soluble in water (0.325 g in 1 l of water at 25°) but is practically insoluble in a saturated solution of lead chloride in cold water. Moreover, in washing the precipitate with water, less of the precipitate dissolves than corresponds to the formation of a saturated solution.

Procedure. Fuse 0.5 g of sample, in a platinum crucible, with about 5 g of sodium carbonate. Leach the cooled melt with hot water and filter when its disintegration is complete. Wash back the insoluble residue into the beaker used for the leaching, add 50 ml of 2 per cent sodium carbonate solution, boil a few minutes, filter, and wash with hot water until a drop of the filtrate is neutral to red litmus paper. The residue will contain a part of the silica in the original sample and must be saved for its determination.

To the combined filtrates, at a volume of about 300 ml, add zinc nitrate solution which has been prepared by dissolving 1 g of zinc oxide in 20 ml of 1.5 N nitric acid. Boil 1 minute and filter off the precipitate. Wash thoroughly with hot water and save this precipitate also for the silica determination.

Add a few drops of methyl red indicator solution to the filtrate and nearly neutralize with nitric acid. Evaporate to about 200 ml, but take care that the solution remains slightly alkaline. After this evaporation, however, add 1.5 N nitric acid until the color of the solution is a very faint pink. Now add an ammoniacal zincate solution prepared by treating 1.0 g of zinc oxide and 2.0 g of ammonium carbonate with 20 ml of water and 2 ml of concentrated NH₄OH and digesting on the water bath until the solution is clear, and heat in a covered platinum dish

[1] Bur. Standards J. Research, 3, 58 (1929).

until there is no more odor of ammonia, which usually requires evaporation to about 50 ml. Add 50 ml of warm water, stir, digest a few minutes, filter, and wash the precipitate with cold water. It contains the last traces of silica, and the filtrate contains all the fluorine.

Determination of Silica. With the aid of a jet of 0.6 N hydrochloric acid, transfer the three precipitates obtained above to the dish in which the last precipitation was made. Ignite the filters and add any residue to the contents of the dish. Now add 25 ml of concentrated hydrochloric acid and evaporate to dryness on the steam bath. Remove the dish from the steam bath, moisten the residue with 10 ml of concentrated hydrochloric acid, warm slightly, and then add 100 to 150 ml of hot water. Digest on the steam bath for 15 minutes, filter, and wash thoroughly with hot dilute 0.6 N hydrochloric acid and then with hot water. Return the filtrate and washings to the dish in which the evaporation was made, add 10 ml of concentrated sulfuric acid, and evaporate until fumes of sulfuric acid are evolved. Allow to cool, add 100 to 150 ml of water, heat carefully until salts are in solution, filter, and wash with hot water. Place the two papers containing the silica in a weighed platinum crucible, heat slowly until dry, next char the paper without inflaming, burn off the carbon at as low a temperature as possible, and finally ignite to about 1000° C. Cool in a desiccator, weigh, and repeat the heating until a constant weight is obtained. Determine the silica by treatment with hydrofluoric and sulfuric acids in the usual manner.

Determination of Fluorine. Take the filtrate from which the three impure silica precipitates were removed and add a few drops of bromophenol blue indicator solution.[1] Adjust the volume of the solution to 250 ml, add dilute nitric acid until the color changes to yellow, and then add dilute sodium hydroxide until it changes just to blue. Now add 2 ml of 6 N hydrochloric acid and 5 g of solid lead nitrate, and heat on the steam bath. As soon as the lead nitrate is in solution, add 5 g of solid sodium acetate, stir vigorously, and digest on the steam bath for ½ hour with occasional stirring. Allow to stand at least 4 hours at room temperature and then decant the solution through a paper filter of close texture. Wash the precipitate, beaker, and paper once with cold water, then 4 to 5 times with a cool saturated solution of lead chlorofluoride, and then once more with cold water.

Transfer the precipitate and paper to the beaker in which the precipitation was made, stir the paper to a pulp, add 100 ml of 0.75 N nitric acid, and heat on the steam bath until the precipitate is dis-

[1] Prepared by triturating 0.4 g of the dry powder with 6 ml of 0.1 N NaOH and diluting to 100 ml.

solved. Then add a slight excess of standard, approximately 0.2 N solution of silver nitrate, carefully noting the volume. Digest on the steam bath for ½ hour, cool to room temperature while protected from the light, filter, wash with cold water, and determine the silver nitrate in the filtrate by means of a standard solution of potassium thiocyanate, using 5 ml of a solution of ferric alum as the indicator.[1]

Determination as Silicon Fluoride

This method, proposed by Fresenius, depends upon the fact that many fluorides are decomposed by the action of concentrated sulfuric acid and silica; the fluorine escapes as silicon fluoride, which can be absorbed and weighed.

Procedure. The same reagents and a very similar apparatus to that described on p. 402 are required for this determination, except that in place of the Péligot tubes (Fig. 67, p. 403) two weighed, glass-stoppered U-tubes are used, of which the first is filled with moistened pieces of pumice, and the second has one arm filled with soda-lime and the other with calcium chloride. The analysis is carried out in exactly the same way as is described for the Penfield method (see p. 402) but at the end of the experiment the two U-tubes are weighed. The increase in weight represents the amount of SiF_4, and from this the amount of fluorine present is calculated as follows: Assume that a g of calcium fluoride yielded p g of SiF_4. The treatment with the concentrated sulfuric acid caused the following reaction to take place:

$$2CaF_2 + 2H_2SO_4 + SiO_2 = 2CaSO_4 + 2H_2O + SiF_4$$
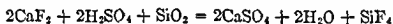
The SiF_4 is caught in the weighed U-tubes but the H_2O is retained in the concentrated H_2SO_4; consequently, $\dfrac{4F \cdot p \cdot 100}{SiF_4 \cdot a} = \dfrac{73.03 p}{a} =$ per cent fluorine present.

Remark. This method is suitable for the determination of fluorine in all fluorides that are decomposed by sulfuric acid. The analysis can be carried out in the presence of phosphates, but if carbonates are present they should be decomposed by ignition before the treatment with sulfuric acid According to K. Daniel, exact results are obtained only when the decomposition of the fluoride takes place at the temperature at which sulfuric acid boils. The method is not suitable for the determination of fluorine in topaz and micas.

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[1] In routine work the determination of fluorine can be made without removing the last traces of silica with ammoniacal zincate solution To apply the above procedure to the analysis of fluorite or other minerals containing little silica, about 0 6 g of pure silica should be added to 0.25 g of the sample before fusing with sodium carbonate at the start of the analysis.

Determination of Fluorine as Fluosilicic Acid, according to
S. L. Penfield. Modified by Treadwell and Koch

Principle. In this method the fluorine is expelled as silicon fluoride exactly as in the above method of Fresenius, but the gas is absorbed in 50 per cent alcoholic potassium chloride solution. By contact with water the silicon fluoride is decomposed into fluosilicic and silicic acids. The former unites with the potassium chloride, forming potassium fluosilicate, insoluble in 50 per cent alcohol:

$$3SiF_4 + 3H_2O \rightarrow 2H_2SiF_6 + H_2SiO_3 \qquad H_2SiF_6 + 2KCl = K_2SiF_6 + 2HCl$$
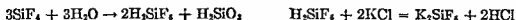
and sets free an equivalent amount of hydrochloric acid which can be titrated with 0.2 N sodium hydroxide solution, using cochineal as an indicator. From the above equations, it is evident that

$$1000 \text{ ml } 0.2 \text{ } N \text{ HCl} = 0.3 \text{ mole CaF}_2$$

$$\therefore 1 \text{ ml } 0.2 \text{ } N \text{ NaOH} = 0.0234 \text{ g CaF}_2 \text{ or } 0.0114 \text{ g F}$$

Requirements. 1. *Pure Quartz Powder.* Place pieces of pure quartz in a platinum crucible, heat strongly over the blast lamp, and then drop into cold water. After this treatment it is very easy to reduce the quartz to a fine powder by grinding in an agate mortar. Ignite the powder, and while still warm transfer to a flask fitted with ground-glass stopper. Allow the open flask and its contents to cool in a desiccator, stopper, and set aside.

2. *Sea Sand.* Treat clean sea sand with boiling concentrated sulfuric acid, wash, dry, ignite, and cool in a desiccator.

3. *Anhydrous Sulfuric Acid.* Heat pure, concentrated sulfuric acid in a porcelain crucible until it is reduced one-third in volume and allow to cool in an empty desiccator.

Procedure. Mix 0.1 g of the dry fluoride in an agate mortar, which is placed upon black glazed paper, with 2 g of the quartz powder, and transfer through the cylindrical arm A of the perfectly dry decomposition apparatus to the pear-shaped compartment B shown in Fig. 67. Then add 1.5–2 g of the sea sand, and mix with the rest of the material by shaking the apparatus. Then make connection with the dry U-tube, D, containing glass beads.[1] Place 15 ml of alcohol saturated with potassium chloride in each of the two Péligot tubes P and P_1. When the apparatus is connected as shown in the drawing, allow a dry current of air,[2] free from carbon dioxide, to enter at h, and pass through the apparatus at the rate of 2 or 3 bubbles per second. Then without stopping the air current, introduce about 20 ml of anhydrous sulfuric acid into the decomposition apparatus through the funnel T. By introducing the sulfuric acid in this way while maintaining the air current,

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[1] This tube serves to keep back any sulfuric acid that is carried over mechanically. The apparatus has been simplified by Rosanov, *Z. anal. Chem.*, 103, 328 (1935).

[2] Wash the air by passing it through caustic potash solution, and dry it by passing through granular calcium chloride and concentrated sulfuric acid.

the sulfuric acid and the greater part of the silica and fluoride mixture are
made to pass directly into the compartment B. After adding the sul-
furic acid, place the decomposition vessel in a paraffin bath and heat
slowly to a temperature of 130° to 140°. The evolution of silicon
tetrafluoride at once begins, as is evident from the formation of foam.
Continue passing air and heating the bath for 5 hours; then turn down
the flame under the bath and pass air through the apparatus for half an
hour longer at the rate of 3-4 bubbles per second. During the heating
the apparatus should be frequently shaken in order to bring the sulfuric
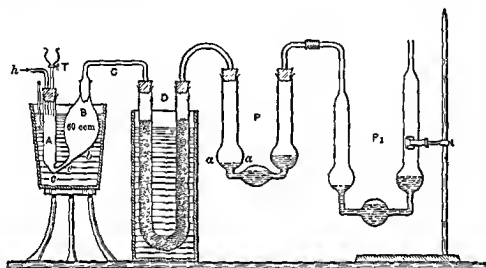
Fig. 67.

acid into contact with all portions of the solid mixture. It is not neces-
sary, however, with this arrangement of the apparatus, to shake as
frequently as in the forms of apparatus described by Penfield and by
Fresenius, because the air in its passage through the narrow connecting
tube between A and B of the decomposition apparatus serves of itself
to effect a good mixing. To accomplish this end, however, it is neces-
sary to construct the apparatus exactly as shown in Fig. 67; the con-
necting tube between A and B must be so narrow that it is completely
filled with the bubbles of air passing, and furthermore the parts marked
$c\ e\ b$ must form an inclined plane upon which the substance can readily
pass back and forth. If there is a hollow in the apparatus at $c\ e\ b$, in
which some of the substance can collect, the sulfuric acid may not come
in contact with some of the fluoride so that the decomposition will be
incomplete. Similarly it is necessary to guard against making the
connecting tube $c\ e$ too narrow, as otherwise the air will not pass in a
uniform stream, but in spurts, so that in spite of the long tube D some

of the sulfuric acid fumes are likely to reach the Péligot tubes and thereby give rise to high results.

If not more than 0.1 g of the fluoride is present, the action is over at the end of 5½ hours, and this is evident, as Daniel[1] was the first to discover, from the fact that the foaming in the apparatus ceases; the hydrochloric acid which has been set free in the Péligot tubes can now be titrated. To this end add a few drops of fresh cochineal[2] solution to each tube and titrate the contents with 0.2 N potassium hydroxide solution with frequent shaking, until the indicator changes from yellow to red. This, however, is by no means the correct end point, because, as Penfield observed, the gelatinous silicic acid encloses very appreciable amounts of hydrochloric acid. The silicic acid, therefore, must be thoroughly worked over with a stirring rod and the addition of the alkali hydroxide continued until the color change is permanent.

Remark. This method is capable of giving excellent results but it is important that the apparatus and all the reagents added to the decomposition vessel should be perfectly dry. Phosphates do not interfere, but carbonates must be removed by a preliminary ignition. If the mineral contains "combined water" there is danger of losing hydrofluoric acid by this ignition, but such loss can be prevented by adding an oxide such as lime or litharge.

The procedure can be modified to apply to the determination of fluoride in native sulfides such as sphalerite.[3] In this case mix 1 g of the substance (dried at 110°), with 2 g of sand and 2 g of anhydrous copper sulfate, and cover with 10 g of anhydrous chromic acid anhydride (CrO_3). After introducing sample and the sulfuric acid, as described above, gradually raise the temperature to 130-140° during 2 hours while passing a current of dry, CO_2-free air through the apparatus, and then heat 3 hours at this temperature.

In early editions of this book, it was proposed to dry the sulfuric acid over phosphorus pentoxide, but such acid evolves a little sulfuric anhydride in the analysis and the results are usually about 0.4 per cent too high.

Determination of Fluorine in Mineral Waters

Evaporate 1–10 l of the water (according to the amount of salts present) to a small volume, in a large dish, adding enough sodium carbonate to keep the solution slightly alkaline. Add an excess of calcium chloride, boil, filter off the precipitate and wash it with hot water until free from chlorides. Dry the precipitate, transfer it as completely as possible to a platinum dish, add the ash of the filter to the main precipitate, and gently ignite. This residue contains all the fluorine as calcium

[1] Z. anorg. Chem., 38, 257 (1904).

[2] Instead of cochineal, methyl orange may be used, although it is necessary then to add an equal volume of alcohol before titrating the hydrochloric acid.

[3] L. da Rocha-Schmidt and K. Krüger, Z. anal. Chem., 63, 29 (1923).

oride, besides considerable calcium (possibly strontium) and magsium carbonates, iron, aluminum, and manganese oxides, often barium
lfate, and almost invariably some calcium phosphate. Moisten it with
excess of dilute acetic acid, allow to stand for some time with frequent
rring, and then evaporate to dryness on the water bath. Treat the
sidue with water, filter, and wash with hot water. Transfer as much
it as possible to a platinum crucible, add the ash of the filter, and
ntly ignite the contents of the crucible. Mix 0.5–1 g of ignited quartz
wder with the residue in an agate mortar. Transfer the mixture to the
composition vessel A, Fig. 67, and treat with concentrated sulfuric
id exactly as described above by the method of Penfield. As only
ry little fluorine is present in this case, two small U-tubes can be used
stead of the large Péligot tubes shown in Fig. 67.

Remark. The formation of a precipitate in the first U-tube at the place marked
in Fig. 67 indicates the presence of fluorine. It is well to confirm it by the etch-
test. After carrying out the titration of the hydrochloric acid set free, transfer
e contents of the U-tube to a platinum dish, add a few drops of $2 N$ sodium car-
nate, and evaporate the solution to dryness. Add ammoniacal zinc oxide (cf.
398), and again remove the liquid by evaporation. Take up the residue in water,
d filter off the zinc oxide and silicate. Treat the filtrate with calcium chloride as
scribed on p. 397, and apply the etching test.

Gas-Volumetric Determination of Fluorine according to Hempel and Oettel

See Part III, " Gas Analysis."

Separation of Fluorine

(a) From the Metals

For the determination of the metals present, the fluorine usually
an be removed by heating with concentrated sulfuric acid. However,
ith many silicates containing fluorine, e.g., topaz, lepidolite, and other
icas, this treatment will not accomplish the desired result. In such
ses fuse the mineral with 4–6 times as much sodium-potassium car-
onate, and remove the silica and aluminum as described on p. 398
y treatment with ammonium carbonate and ammoniacal zinc solution.
se the precipitates for the determination of aluminum and silica
d the filtrate for the determination of the fluorine. The alkalies
ust be determined in a separate portion of the original substance
pp. 416, 418).

(b) Separation of Fluorine from the Acids

1. *Determination of Hydrochloric and Hydrofluoric Acids in the Presence of One Another*

With soluble alkali salts, precipitate the fluorine from the solution by means of a little sodium carbonate and an excess of calcium nitrate solution, as described on p. 397. Make the filtrate acid with nitric acid and determine the chlorine by precipitation with silver nitrate, according to p. 291.

It is simpler to treat the solution containing hydrochloric and hydrofluoric acids in a platinum evaporating dish with nitric acid and silver nitrate. Silver chloride is alone precipitated and can be filtered off, using a funnel of hard rubber or a glass one coated over with wax. Wash the precipitate and weigh as described on p. 291. When phosphoric acid also is present, precipitate it with the chloride by the addition of silver nitrate to the slightly alkaline solution. Filter off the precipitate, wash with as little cold water as possible, and treat the precipitate with dilute nitric acid. By this means the silver phosphate goes into solution, while the silver chloride is unaffected. To determine the amount of phosphoric acid present, remove the silver from the solution by the addition of hydrochloric acid, and precipitate phosphoric acid in the filtrate by addition of magnesia mixture and ammonia (cf. p. 370).

In the filtrate from the silver phosphate and silver chloride precipitate, remove the excess of silver nitrate by the addition of sodium chloride and determine the fluorine as calcium fluoride.

In the case of an insoluble compound containing chlorine and fluorine, extract the melt obtained after fusing with sodium-potassium carbonate with water, remove the silica with ammonium carbonate and ammoniacal zinc solution as described on p. 398, and determine the chlorine and fluorine as above.

Usually it is more convenient to determine the two acids in separate portions of the substance.

2. *Determination of Boric and Hydrofluoric Acids*

To the solution containing the alkali salts of these two acids add an excess of calcium chloride at the boiling temperature. Filter off and wash with hot water.

Gently ignite the precipitate, consisting of calcium carbonate, calcium fluoride, and some calcium borate, treat with dilute acetic acid, evaporate to dryness, and add more acetic acid and water. By this

means the calcium acetate and calcium borate go into solution, while the calcium fluoride is left behind and can be determined as described on p. 397. For the boric acid determination take a second portion of the solution, make barely acid with acetic acid, and treat with a slight excess of calcium acetate solution to precipitate the fluorine. Place the solution, together with the calcium fluoride precipitate, in the Gooch retort and subject to distillation as described on p. 365.

FLUOSILICIC ACID, H_2SiF_6. Mol. Wt. 144.08

Forms: Calcium Fluoride, CaF_2; Potassium Fluosilicate; or volumetrically

1. Determination as Calcium Fluoride

Principle. Alkali fluosilicates are decomposed on heating with sodium carbonate solution into fluoride and silicic acid:

$$Na_2SiF_6 + 2Na_2CO_3 + H_2O = 6NaF + H_2SiO_3 + 2CO_2$$
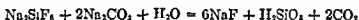
If a solution to be analyzed contains free fluosilicic acid or its sodium salt, add sodium carbonate solution until the reaction is alkaline and then a considerable amount of ammonium carbonate. Heat the solution to about 40°, and, after allowing to stand for 12 hours, filter off the precipitated silicic acid.

The solution now contains all the fluorine as sodium fluoride, in the presence of small amounts of silicic acid, which can be precipitated by the addition of ammoniacal zinc solution (see p. 398). In the filtrate determine the fluorine as calcium fluoride, as described on p. 397.

Fuse an insoluble fluosilicate with 4 times as much sodium-potassium carbonate, extract the melt with water, and subject the solution to the above treatment.

2. Determination as Potassium Fluosilicate

This analysis is applicable only for the determination of free fluosilicic acid in aqueous solution.

Procedure. Treat the solution with potassium chloride and an equal volume of absolute alcohol. Filter off the barely visible potassium fluosilicate through a tared filter which has been dried at 100°. After washing with 50 per cent alcohol dry the precipitate at 100° and weigh as K_2SiF_6.

The volumetric determination of fluosilicic acid will be discussed in Chapter XIV.

Analysis of Salts of Fluosilicic Acid

For the determination of the metal present, treat the salt with concentrated sulfuric acid in a platinum dish and heat until dense fumes

of sulfuric anhydride are given off; silicon fluoride and hydrofluoric acid volatilize, while the metals are left behind as sulfates (cf. Vol. I).

Determination of Water Present in Fluosilicates (Rose-Jannasch)[1]

The water cannot be determined by ignition, because all fluosilicates, even topaz, evolve silicon fluoride when subjected to this treatment (cf. Vol. I). If, as proposed by Rose, the substance is fused with 6 to 8 times as much lead oxide, all the water is evolved, while the fluorine remains behind:

$$R_2SiF_6 + 3PbO = 2RF + 2PbF_2 + PbSiO_3$$

The analysis is best performed according to the directions of Jannasch: Blow a bulb with a capacity of about 25 ml near one end of a tube of difficultly fusible glass which is 26 cm long and 1 cm wide. Near the middle of the longer side of the tube, between asbestos plugs, place a layer 3–5 cm long of pulverized, anhydrous lead oxide, and connect this end of the tube with two weighed calcium chloride tubes. Place the substance in the bulb, add 6–8 times as much lead oxide, and mix with the substance by carefully revolving the tube. Conduct a dry current of air through the apparatus and slowly melt the contents of the bulb. All the water and often some of the fluorine is thereby expelled, and the fluorine is absorbed by the layer of lead oxide. At the end of the operation cautiously heat this layer with a moving flame until no more water condenses in the cooler part of the tube. When all the water has been driven over into the calcium chloride tubes, weigh them with the customary precautions.

[1] Rose-Finkener: *Lehrbuch der analyt. Chem.*, Vol. II, and Jannasch, *Praktischer Leitfaden der Gewichtsanalyse.*

SILICIC ACID (ALSO TANTALIC AND COLUMBIC ACIDS)

SILICIC ACID, H_2SiO_3.   Mol. Wt. 78.08

Form: Silicon Dioxide, SiO_2

Two cases must be considered:

(a) The silicate is decomposed by acids.

(b) The silicate is not decomposed by acids.

(a) Silicates Decomposed by Acids

Weigh out 0.5 g of the powdered silicate into a porcelain dish, add 25 ml of water, and stir till the silicate is thoroughly wet. Add in small portions, while heating the casserole and stirring, 25 ml of 6 N hydrochloric acid. Evaporate upon the water bath with frequent stirring until the residue is obtained in the form of a dry powder. In many cases the decomposition is shown to be complete by the fact that no gritty particles can be felt with the stirring rod on the bottom of the dish. If, however, the substance contained quartz or some silicate that is not decomposed by hydrochloric acid, this is not the case and the procedure described on p. 411 should be followed. Heat the residue for at least an hour in the hot closet at 120–130°, to dehydrate the silica.

Moisten the dry powder with concentrated hydrochloric acid, and allow the covered dish to stand for 10 minutes at the ordinary temperature in order that basic salts and oxides formed during the evaporation and drying may once more be changed to chlorides. Then warm gently, dilute with 100 ml of water, heat to boiling, and, after the silicic acid has settled, filter through a well-fitting ashless paper filter. Wash the residue three or four times by decantation, with hot 2 N hydrochloric acid, then transfer to the filter and wash with hot water until free from chloride. Place the precipitate in a platinum crucible and set aside for the time being. The separation of the silicic acid is not quite complete; as much as 2 mg may remain in the filtrate. To remove this, once more evaporate the solution to dryness on the water bath, and again heat at 120–130°, for an hour, moisten the residue with 5 ml of concentrated hydrochloric acid, and allow to stand not more than 15

409

minutes.[1] Warm, dilute to 100 ml, heat to gentle boiling, and filter
through a new and correspondingly small, ashless filter, washing with hot
2 N acid and with water as before.   Combine this filtrate with that previ-
ously obtained and analyze it for Fe_2O_3, Al_2O_3, CaO, and MgO as de-
scribed on p. 414.   Ignite the wet filters containing the silica in a plati-
num crucible.   Keep the temperature low till all the carbon is consumed,
and do not allow the filter to catch fire.   Finally cover the crucible, and
ignite over the blast lamp or over a Méker burner.

Remark. It is not advisable to use suction in filtering silicic acid. If the pre-
cipitate is allowed to dry before being placed with the filter there is
danger of losing some of the fine powder. The heating at 120° decreases the solubility
of the silica in acid, but this temperature should not be exceeded. Magnesia at a
higher temperature recombines with silica, and iron and aluminum oxides are formed
in a condition hard to dissolve.

Testing the Purity of the Silica

The silica thus obtained is never absolutely pure, except in the analy-
sis of a water-glass.   Its purity must always be tested.   For this pur-
pose moisten it with water;[2] then add a drop of concentrated sulfuric
acid and about 5–10 ml of pure hydrofluoric acid.   Do not measure the
acid in a glass graduate; do not inhale the fumes any more than is neces-
sary; and if any hydrofluoric acid is spilled on the hands wash them
immediately under the water tap.   Place the crucible in an air bath
and evaporate under a good hood until no more vapors are expelled.
Then remove the excess of sulfuric acid by heating over a free flame.
Raise the temperature gradually, and finally heat the crucible over a
blast lamp or Méker burner, and again weigh.   Repeat the treatment
with sulfuric and hydrofluoric acids, without adding any more water,
until the contents of the crucible (usually Al_2O_3, Fe_2O_3, TiO_2, ZrO_2,
V_2O_5, P_2O_5, etc.) are at a constant weight.   Deduct this amount from
the weight of impure silica and add it to the precipitate obtained with
ammonia in the subsequent analysis.   The precipitate of Fe_2O_3, Al_2O_3,
etc., should then be tested for SiO_2 by fusing the weighed precipitate
with $KHSO_4$, treating the melt with dilute sulfuric acid, filtering, and
testing the residue with hydrofluoric acid.

A great many silicates are incompletely decomposed, if at all, by direct treatment
with hydrochloric acid in an open vessel. Inasmuch as it is necessary to test the
purity of the silica by treatment with sulfuric and hydrofluoric acids, it might seem

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[1] By being kept in contact with the acid for too long a time some silicic acid will
go into solution.

[2] If the water is not added, the mass will effervesce so strongly that there is danger
of losing some of the impure silica.

treated with sulfuric and hydrofluoric acids, the alkali and alkaline earths are left as sulfates, the iron is left as Fe_2O_3, and the manganese as Mn_3O_4. Moreover, boron is volatilized as BF_3. Only when the silica is nearly pure and when the impurities are left as oxides in the same state of oxidation as at the start, and no other volatile constituent is present, does the loss in weight upon treatment with hydrofluoric and sulfuric acids represent the silica content. If the silicate is only partly decomposed with acid it should be treated as an insoluble silicate.

(b) Silicates Not Decomposed by Acids

Silicates not decomposed completely by the action of 6 N hydrochloric acid are usually fused with sodium carbonate which converts them partly into sodium silicate and partly into an ortho- or metasilicate which can be decomposed with acid.

Fusion with Sodium Carbonate

Fuse 0.5 g of the very finely powdered substance in a platinum crucible with 3 g of sodium carbonate. The powdered silicate should be intimately mixed with the flux and a little sodium carbonate sprinkled on top. Heat the covered crucible at first over a small flame to drive out any moisture present. Gradually raise the temperature until finally the highest heat of a good Tirrill or Méker burner is obtained. As soon as the mass melts quietly and there is no further evolution of carbon dioxide, the decomposition is complete. Wind a piece of platinum wire into a spiral and insert it into the fused mass. Remove the flame, allow the crucible to cool in the air somewhat and then play a stream of water upon the outside of the crucible. As soon as the crucible does not hiss when the water strikes it, quickly introduce enough water into the crucible to cover the melt. After about a minute carefully pull on the wire; usually the melt can be withdrawn from the crucible. If it does not come out easily, it can often be loosened by carefully heating the crucible.[1] Place the melt in a 300-ml casserole, add 25 ml of water, cover the casserole, and carefully add 25 ml of 6 N hydrochloric acid. A lively evolution of carbon dioxide at once takes place, but as the silicic acid separates, the inner part of the cake gradually becomes coated with a film of silicic acid which protects it from the further action of the acid. Consequently it is necessary to break up the cake from time to time, by means of a glass rod, until finally there is no further evolution of a gas and no more hard lumps remain. When manganese is present the melt

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[1] If the fusion cannot be removed from the crucible, place it, together with its cover, in the beaker, and treat with dilute acid as described

is colored green with manganate and the solution may be pink at first with permanganate but the permanganate gradually decomposes during the subsequent heating. After the evolution of carbon dioxide has nearly ceased, wash off the under side of the watch glass, raise it by placing a glass triangle under it, and evaporate to dryness. Heat the residue for at least an hour in the hot closet at 120–130°, to dehydrate the silica. Continue as described on p. 409.

Effect of Fluoride. Substances containing considerable fluorine cannot be treated as above, for silicon fluoride will be lost by volatilization. Therefore it is necessary to use the old method of Berzelius. Extract the melt from the sodium carbonate fusion with water, as in the determination of fluorine (p. 398), and remove the greater part of the silica by means of ammonium carbonate. Filter off the precipitate, ignite, and weigh.

Precipitate the silicic acid remaining in the filtrate by means of ammoniacal zinc solution (p. 398). Dissolve this precipitate of zinc oxide and zinc silicate in hydrochloric acid and obtain the silica by evaporation on the water bath as usual. As a rule, the insoluble part of the melt contains silicic acid, and this must also be removed by evaporation with hydrochloric acid. Ignite all three silica precipitates together and test the purity of the silica.

ANALYSIS OF SILICATES

Orthoclase, $KAlSi_3O_8$

Constituents: silicic acid (63–70 per cent); aluminum oxide (16–20 per cent); ferric oxide (0.3 per cent); potassium oxide (8–16 per cent); sodium oxide (1–6 per cent); and often small amounts of calcium oxide, magnesium oxide, and in rare cases barium and ferrous oxides.
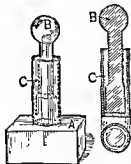
Preparation of the Substance for Analysis

FIG. 68.

Break up large pieces of rock on a thick steel plate with a specially hardened surface and a similarly hardened pounder, such as street pavers use. Place the small fragments in a "diamond" mortar or in one like that shown in Fig. 68. It is made of chilled and case-hardened tool steel. The dimensions of the block A are 12.5 by 12.5 by 6 cm, and there is a depression in the center 0.6 cm deep. The pestle B is 20 cm high, and the diameter at the base is 3.5 cm. The cylinder C is 12.5 cm tall and of 5-cm outside diameter accurately fitting the de-

pression in the block. Unlike the ordinary "diamond" mortar, the pestle has a smaller diameter than the inside diameter of the cylinder, which is 4.4 cm. The crushing is done with the pestle, without the aid of a hammer. With this mortar most of the sample can be reduced fine enough to pass through silk bolting cloth.

A finer powder can be obtained by hand grinding in an agate mortar, but the McKenna ore grinder shown in Fig. 69 is more economical in the long run. A is a copper cup soldered to the head of the pestle holder and assumes, without friction, the motion of the latter. B is a tin plate with deep sinus and is covered by the rubber cloth C which fits closely about the metal shaft. These attachments A, B, and C prevent oil and dust from the belts and bearings from entering the mortar. The spring at the top of the sliding rod, to which the agate mortar is attached at
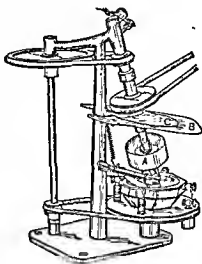
Fig. 69.

the bottom, can be adjusted to give any desired pressure or can be thrown back to allow the pestle to be raised in removing the agate mortar. The pestle makes about 200 revolutions per minute, and the mortar moves slowly in the same direction. The scraper keeps the material in the center, and the combined rolling and sliding motion reduces the hardest ore very quickly.

Do not attempt to grind too much at one time, and frequently sift through silk bolting cloth to prevent as much as possible contaminating the sample by abrasion and loss of moisture by the heat of grinding. Prepare at least 5 times as much sample as is needed, and make sure that all the powder is included; it is never admissible to take only the powder that passes through the sieve the first time. Mix well by rolling on a sheet of glazed paper, rubber, or oilcloth. A corner of the sheet is lifted and drawn across, low down, in such a way that the material is made to roll over and over and does not merely slide along. The sample should be rolled back and forth along each diagonal for 100 times or more. Then the sample may be spread out into squares and a little taken from each square. Finally mix the sample chosen.

Weighing the Substance. It was formerly the practice to dry the powder before weighing at 100–110° until a constant weight was obtained. If there is danger of losing combined water by this procedure, it has been recommended that the powder be dried in a vacuum over con-

centrated sulfuric acid. The practice of drying the substance in either of the above ways, however, is to be discountenanced. It is far better to use the air-dried substance for the analysis, and to determine the moisture in a separate sample. This is more accurate, because the dry silicate powder is hygroscopic, so that a portion weighed out today is likely to contain a different amount of moisture from one taken tomorrow, and this discrepancy is avoided when the air-dried powder is taken for the analysis. Further, as Hillebrand has conclusively shown, chemically combined water is likely to be expelled not only by heating at 100° but also by drying in a vacuum over sulfuric acid. This is particularly true of the zeolites. In orthoclase, however, only about 0.1 per cent of moisture is present, so that with this particular substance accurate results will be obtained by either method.

For the analysis weigh out to the nearest 0.1 mg four portions of about 0.5 g each. The first two serve for the determination of SiO_2, Al_2O_3 + Fe_2O_3, CaO, and MgO; the other two, for that of the alkalies.

Determination of Silica, Aluminum, etc.

Weigh out 0.5 g of the air-dried substance in a spacious platinum crucible, dry for 1 hour at 105–107°, cool in a desiccator, and weigh. The difference in weight represents the amount of hygroscopic moisture.

Mix the dry substance with 3 g of calcined sodium carbonate by means of a platinum spatula, and determine silica as described on p. 411. Treat the silica with sulfuric and hydrofluoric acids, as described on p. 410, and set the crucible with the residue of Al_2O_3, etc., aside for the present.

Determination of Aluminum and Ferric Oxides

The filtrate from the silicic acid contains, besides the chlorides of aluminum, iron, calcium, and magnesium, a little platinum, from the crucible in which the fusion was made.

To remove the platinum, heat the solution to boiling and introduce hydrogen sulfide. Filter off the mixture of platinum sulfide and sulfur, and boil the solution to expel the excess of hydrogen sulfide. Oxidize the iron back to the ferric state by adding bromine water and boiling until the excess of the latter is expelled. After this add 10 ml of 2 N ammonium chloride solution and precipitate the aluminum, iron, etc., from the boiling-hot solution, by the addition of a slight excess of ammonia, free from carbonate (cf. p. 206). Allow the precipitate to settle, filter, and wash twice by decantation with hot water. Redissolve by running hot 2 N hydrochloric acid through the filter into the beaker

containing the greater part of the precipitate.   Repeat the precipitation with ammonia as before, and after filtering and washing by decantation, transfer the precipitate to the filter and wash until free from chloride with water containing 2 per cent of ammonium nitrate.   Allow the precipitate to drain as completely as possible, and ignite wet in the crucible containing the residue obtained from the treatment of the impure silica with sulfuric and hydrofluoric acids.   After igniting strongly over a good Teclu or Méker burner weigh the crucible; its contents represent the sum of the aluminum and ferric oxides (also TiO_2, ZrO_2, P_2O_5, and V_2O_5, if present).

For the determination of the ferric oxide, fuse the mixed oxides with potassium pyrosulfate as described on p. 174.   The decomposition is complete after 2–4 hours.   Dissolve the melt in water containing a little sulfuric acid and determine the iron, after previous reduction with hydrogen sulfide (cf. p. 172), by titration with potassium permanganate (cf. Chapter XV).   If the weight of the Fe_2O_3 is deducted from the weight of $Fe_2O_3 + Al_2O_3$, the weight of Al_2O_3 is obtained.[1]   Determine the calcium and magnesium as described on pp. 263, 266.

Testing the Calcium Oxalate Precipitate for Barium

Although it is usually unnecessary to make either a qualitative or quantitative test for barium in a sample of orthoclase, yet it is likely to be present in traces so that it may be well to show how this can be done.   Strontium is not likely to be found in orthoclase.   On account of the solubility of barium oxalate in a solution of ammonium oxalate, the barium will rarely be found in the calcium precipitate when a double precipitation is made, except when it is present to an extent of more than 3 or 4 mg.[2]

To test a calcium precipitate for barium, dissolve it in nitric acid, evaporate to dryness, and heat for some time at 140°.   Dissolve the calcium nitrate in ether-alcohol (p. 251, a), and examine any residue remaining behind in the spectroscope for barium.   If barium is found, dissolve in dilute acid and repeat the precipitation with ammonia and ammonium oxalate.   If no barium is found with the lime, it is by no

[1] The amount of iron and aluminum can be determined more quickly, though less accurately, as follows: Dissolve the moist ammonia precipitate in hot, dilute sulfuric acid and dilute to a volume of exactly 250 ml.   After thoroughly mixing, remove 100 ml by means of a pipet into a beaker and place a second portion of the same volume in a 200-ml flask.   In the first portion determine the sum of $Fe_2O_3 + Al_2O_3$ by precipitating with ammonia, filtering, igniting, and weighing; in the other portion reduce the iron by hydrogen sulfide and titrate with permanganate.

[2] W. F. Hillebrand, *J. Am. Chem. Soc.*, **16**, 83 (1894).

means safe to conclude that barium is absent; it can very well have gone into the filtrate from the double precipitation of calcium. This amount will be precipitated with the magnesium as barium phosphate unless it is removed as indicated below.

For the quantitative determination of barium a separate portion of the substance should be taken (see below).

Determination of Barium

If the qualitative tests have shown the presence of barium, weigh out 2 g of the substance into a platinum dish; moisten with 10 ml of 7 N sulfuric acid and 5 ml of hydrofluoric acid. Evaporate the liquid on the water bath, with frequent stirring, until the mineral is completely decomposed, when sandy particles will no longer be perceptible on stirring with a platinum spatula. Frequently a further addition of hydrofluoric acid is necessary. When the decomposition is complete, remove the greater part of the sulfuric acid by heating the contents of the dish in an air bath. After cooling, take up the residue in water, filter off the barium sulfate, and ignite wet in a platinum crucible. The precipitate thus obtained always contains small amounts of calcium sulfate which must be eliminated. To accomplish this, dissolve the residue in the crucible in a little hot concentrated sulfuric acid, and after cooling, dilute the solution with cold water. The barium sulfate is now completely free from calcium; filter, ignite again, and weigh.

Determination of the Alkalies

(a) Method of J. Lawrence Smith[1]

Principle. The substance is heated with a mixture of 1 part ammonium chloride and 8 parts calcium carbonate. By this means the alkalies are obtained in the form of chlorides, while the remaining metals are for the most part left behind as oxides (silicates and aluminates), and the silica is changed to calcium silicate, as represented by the following equations:

$$CaCO_3 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3 + H_2O + CO_2$$
$$2KAlSi_3O_8 + CaCl_2 + 6CaCO_3 \rightarrow 6CaSiO_3 + Ca(AlO_2)_2 + 2KCl + 6CO_2$$
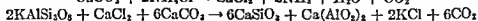
The alkali chlorides together with the excess calcium chloride can be removed from the sintered mass by leaching with water, while the other constituents remain undissolved.

Preparation. The ammonium chloride necessary for the determination is prepared by subliming the commercial salt; the calcium carbonate by dissolving the purest calcite obtainable in hydrochloric acid and precipitating with ammonia and ammonium carbonate. Carry out this last operation in a large porcelain dish.

[1] Am. J. Sci., [2] 50, 269, and Ann. Chem. Pharm., 159, 82 (1871).

After the precipitate has settled, pour off the clear solution and wash the precipitate by decantation until free from chlorides. The product thus obtained contains traces of alkalies, but the amount present can be determined once for all by a blank test and a corresponding deduction made from the results of the analysis; it is usually sodium chloride and amounts to 0·0012–0·0016 g for 8 g calcium carbonate. The decomposition was performed by Smith in a finger-shaped crucible about 8 cm long and with a diameter of about 2 cm at the top and 1½ cm at the bottom. Such a crucible is suitable for the decomposition of about 0·5 g of the mineral. A larger quantity can be analyzed in a somewhat wider crucible.

Filling the Crucible. Mix 0.5 g of the mineral (accurately weighed) with an equal quantity of sublimed ammonium chloride by trituration in an agate mortar, add 3 g of calcium carbonate, and intimately mix again. Transfer the mixture to a platinum crucible with the help of a piece of glazed paper, rinse the mortar with 1 g of calcium carbonate, and add this to the contents of the crucible.

The Ignition. Place the covered crucible in a slightly inclined position and heat gradually over a small flame until no more ammonia is evolved (this should take about 15 minutes). During this part of the operation the heat should be kept so low that ammonium chloride does not escape. The latter is dissociated into ammonia and hydrochloric acid by the heat, and the acid unites with the calcium carbonate to form calcium chloride. It is possible to decompose the silicate by using calcium chloride alone. Gradually raise the temperature until finally the lower three-fourths (and no more) of the crucible is brought to a dull red heat, and maintain this temperature for 50–60 minutes. Then allow the crucible to cool; the sintered cake usually can be removed by gently tapping the inverted crucible. If it cannot, digest a few minutes with water, which serves to soften the cake so that it can be readily washed into a large porcelain, or, better, platinum dish. Heat the covered dish with 50–75 ml of water for half an hour, replacing the water lost by evaporation and reducing the larger particles to a fine powder by rubbing with a pestle in the dish. Decant the clear solution through a filter and wash the residue 4 times by decantation, then transfer to the filter and wash with hot water until a few milliliters of the washings give only a slight turbidity with silver nitrate. To make sure that the decomposition of the mineral has been complete, treat the residue with hydrochloric acid; it should decompose completely, leaving no trace of undecomposed mineral. The acid usually gelatinizes silica; the formation of a gelatinous precipitate does not indicate incomplete decomposition.

Precipitation of the Calcium. To the aqueous solution add 50 ml of ammonium carbonate reagent, heat nearly to boiling, and filter. Evaporate the filtrate to dryness in a porcelain or platinum dish, heat the

contents of the dish for an hour in a drying oven at 110°, and remove
ammonium salts by careful ignition over a moving flame. After cooling,
dissolve the residue in a little water and remove the last traces of cal-
cium by the addition of ammonia and ammonium oxalate to the hot
solution. After standing 12 hours, filter off the calcium oxalate and
receive the filtrate in a weighed platinum dish, evaporate to dryness,
and gently ignite. After cooling, moisten the mass with hydrochloric
acid to transform any carbonate into chloride, repeat the evaporation
and ignition, and determine the weight of the dish and its contents;
this shows the amount of alkali chloride present.

Continue as indicated on p. 281.

(b) The Hydrofluoric Acid Method of Berzelius

Weigh 0.5 g of the powdered mineral into a platinum dish, moisten
with 2 ml of water and 0.5 ml of concentrated sulfuric acid, mix with
the substance by means of a platinum spatula, and after cooling add
about 5 ml of pure, concentrated hydrofluoric acid. Evaporate the
liquid on the water bath, frequently stirring with the platinum spatula,
until no more hydrofluoric acid is expelled and no more hard particles
can be felt at the bottom of the dish.

Heat the dish in an air bath until the greater part of the sulfuric
acid is removed; this is necessary to make sure that the hydrofluoric
acid is completely expelled. It is not advisable, however, to remove
all the sulfuric acid, on account of the danger of forming insoluble
basic salts. Allow the mass to cool, cover with 200 ml of water, and
digest until all the residue has gone into solution.[1] Transform the
sulfates to chlorides by precipitation with as slight an excess of barium
chloride as possible; and then, without stopping to filter off the barium
sulfate, precipitate the aluminum, calcium, and excess of barium by
the addition of ammonia and ammonium carbonate. Allow the pre-
cipitate to settle, wash 4 times by decantation, then transfer to the
filter and wash free from chloride. Evaporate the filtrate to dryness,
heat for an hour at 120°, and remove the ammonium salts by gentle
ignition. Add a few drops of 6 N hydrochloric acid, and remove the
magnesium by the Schaffgottsche method described on p. 289. In the
filtrate determine sodium and potassium as described on p. 281.

Remark. This method is in very general use, and the results obtained agree
closely with those by the J. Lawrence Smith method. Many silicates, such as the
feldspars, are readily decomposed by the action of sulfuric and hydrofluoric acids;[2]

[1] If barium was present, it is left behind as the sulfate.
[2] Many silicates can be decomposed by evaporation with hydrofluoric and hydro-
chloric acids. F. Hinden, Z. anal. Chem., 1906, 332;

others, such as certain specimens of tourmaline, only with difficulty. According to Jannasch the members of the andalusite group are not completely decomposed by hyrofluoric acid, but complete decomposition can be effected by strongly igniting with ammonium fluoride. For this purpose place the ignited mineral in a platinum dish, cover with 10 ml of ammonia, evaporate to dryness, dilute with water, strongly acidify with concentrated hydrofluoric acid, and again evaporate to dryness. Place the dish in a nickel beaker and ignite quite strongly, until finally the excess of ammonium fluoride is driven off. Now treat the residue with 12 N sulfuric acid to decompose salts of fluosilicic acid, evaporate on the water bath as far as possible, and remove then the greater part of the sulfuric acid by stronger ignition. From this point the procedure is the same as in the regular Berzelius method

The Smith method is always applicable and has the advantage that the magnesium is practically completely removed at the start.

Determination of Silicon in Iron and Steel

Silicon exists in cast irons and steels chiefly as a solid solution of Fe_2Si in iron. In wrought iron and in some steels, a little silicate of Fe or Mn may be present, such as $Mn_2Si_2O_6$; this really represents enclosed slag. The compound FeSi has also been identified in Fe-Si alloys. In cast irons, the silicon has a marked effect in causing the breaking down of cementite, Fe_3C, into Fe and graphite. With increasing Si content, the graphite increases, but this effect is counterbalanced by the effect of S so that, roughly speaking, a given percentage of S neutralizes a definite percentage of Si.

Although Si enters into salts as silicate ion and not as Si^{++++} ions, the free element and its compounds with iron are oxidized very easily so that decomposition with any acid will cause oxidation of the Si to the quadrivalent state with evolution of hydrogen gas. There is, therefore, no loss of volatile silicon hydride when a sample of steel is dissolved in hydrochloric or sulfuric acid. If, however, nitric acid or other oxidant is used, the more powerful oxidizing agent is reduced without any evolution of hydrogen.

$$FeSi + 2H^+ + 3H_2O \rightarrow Fe^{++} + H_2SiO_3 + 3H_2 \uparrow$$
$$Fe_2Si + 4H^+ + 3H_2O \rightarrow 2Fe^{++} + H_2SiO_3 + 4H_2 \uparrow$$
$$3Fe_2Si + 28H^+ + 10NO_3^- \rightarrow 6Fe^{+++} + 10NO \uparrow + 3H_2SiO_3 + 11H_2O$$
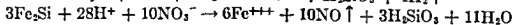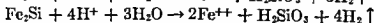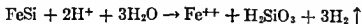
In these reactions the product is really $SiO_2 \cdot xH_2O$ rather than exactly H_2SiO_3.

The following method[1] is excellent for the determination of silicon. Perchloric acid is used instead of sulfuric acid[2] because anhydrous perchlorates are easily soluble and there is no difficulty in dissolving the

[1] Willard and Cake, *J. Am. Chem. Soc.*, **42**, 2208 (1920).
[2] T. M. Drown, *Trans. Am. Inst. Mining Eng.*, **7**, 346 (1878–79).

salts after the silica has been dehydrated. Chromium is oxidized to chromic acid and remains in solution. The chief precautions are to add sufficient perchloric acid to keep the mixture liquid after the nitric acid has been expelled and to boil at least 15 minutes at this stage in the analysis.

Procedure. Treat 2.336 g of sample (5 times the factor weight) with 40 ml of 6 N HNO_3 in a 400-ml covered beaker. When the sample is entirely decomposed, rinse and remove the watch-glass cover and add 40 ml of 60–70 per cent $HClO_4$. Evaporate to fumes of $HClO_4$. Replace the watch glass on the beaker, and heat so that the $HClO_4$ condenses and runs down the sides of the beaker for 15 minutes, but do not allow the contents of the vessel to become pasty or solid. Cool somewhat, and dilute with 125 ml of hot water. Stir until the salts have dissolved, and crush any lumps with a glass stirring rod. Filter and transfer all the residue to an ashless filter paper with the aid of 0.6 N HCl, scrubbing the beaker with a rubber policeman. Wash alternately with 5-ml portions of hot 0.6 N HCl and of hot water until all the iron salts have been removed. The washing must be done carefully as residual $HClO_4$ may cause loss of material in the subsequent ignition of the precipitate. Transfer the paper and residue to a weighed platinum crucible, and ignite slowly and carefully until all the carbon is gone. Cool in a desiccator, and weigh the impure SiO_2. Moisten the residue with 18 N H_2SO_4 and add (without measuring) about 5 ml of HF. Heat inside an air bath until all H_2SO_4 is expelled, and then heat the crucible strongly over a free flame. Cool in a desiccator and weigh. The loss in weight represents the SiO_2, and, when the above weight of sample is taken, this loss multiplied by 20 gives the percentage of Si present.

Determination of Ferrous Iron in Silicates and Rocks

Place 0.5–1.0 g of the fine powder in an 80–100 ml platinum crucible, cover with water, and add 10 ml of 9 N sulfuric acid, cautiously if any carbonate is present. Add air-free hot water till the crucible is nearly half full. Place the crucible, with its cover on, on a triangle near a very low flame protected from drafts. Displace the air in the crucible by introducing a stream of carbon dioxide through a small tube placed under the cover of the crucible. In a short time the liquid in the crucible boils, but before this happens stop the current of gas and drop the crucible cover in place. From a small platinum crucible held in one band, while the other draws the crucible cover to one side, add 5–7 ml of hydrofluoric acid. Quickly replace the lid and increase the heat but take care not to let the liquid boil over. As soon as steam issues, lower the flame and keep so that there is steady boiling without danger

of loss for about 10 minutes. Then transfer the crucible, without removing the cover, to 200 ml of cold, saturated boric acid solution.

Remove the crucible with a stirring rod, rinse it out and titrate at once with permanganate, added rapidly until the first pink blush appears throughout the whole liquid.

If an unattacked residue remains in the beaker, filter it off and repeat the above treatment.

Another method for the determination of the amount of ferrous iron present in insoluble silicates is that of Mitscherlich. The silicate is decomposed in a closed tube with sulfuric acid ($8H_2SO_4 \cdot 1H_2O$) under pressure, and the resulting solution titrated with potassium permanganate. This method usually gives good results in a silicate analysis, but it is worthless for the analysis of rocks containing pyrite or other sulfides, which on treatment with sulfuric acid are decomposed.[1] The sulfur serves to reduce iron that was originally present in the ferric form, so that a high result is obtained.

Separation of Soluble from Insoluble Silicic Acid: Lunge and Millberg[2]

Frequently a mixture of silicates is to be analyzed which is partly decomposed on treatment with acids, with the separation of gelatinous silicic acid, and partly unaffected. The silicic acid deposited from solution by the addition of acids is soluble in 5 per cent sodium carbonate solution, while quartz and feldspar are not appreciably attacked by the latter (cf. Vol. I).

If it is desired to separate the deposited silicic acid from the unattacked silicate (usually feldspar and quartz), treat the substance with acid (hydrochloric or nitric) and evaporate on the water bath until a dry powder is obtained. Moisten this with acid, dilute, boil, and filter. After washing, digest the residue with 5 per cent sodium carbonate solution on the water bath, in a porcelain dish for 15 minutes. Filter; wash the residue first with soda solution and finally with water.

The alkaline filtrate contains the soluble silicic acid; this can be determined by acidifying and evaporating to dryness. The residue from the sodium carbonate treatment, consisting of quartz and feldspar, is weighed. To determine the quartz, treat with sulfuric and hydrofluoric acids, remove the excess of the HF by heating to fumes of sulfuric acid, and dissolve the cold residue in water. In this solution precipitate the alumina, as described on p. 148, and weigh the Al_2O_3. If this weight

[1] L. L de Koninck, *Z. anorg. Chem.*, **26**, 125 (1901); Hillebrand and Stokes, *J. Am Chem. Soc.*, 22, 625 (1900); Stokes, *Am. J. Sci.*, Dec, 1901.

[2] *Z. angew. Chem.*, 1897, 393, 425.

is multiplied by 5.46, the corresponding amount of feldspar is obtained; and if this is deducted from the weight of the quartz + feldspar, the weight of the quartz will be found.

Determination of Soluble Silicic Acid in Clay

Clay contains, besides alumina, sand (quartz + breccia), and small amounts of calcium and magnesium carbonates.

Moisten 2 g of the coarsely powdered substance, which has been dried at 120°, with water, and add 150 ml of 12 N sulfuric acid.[1] Cover the porcelain dish with a watch glass and heat over a free flame until dense fumes of sulfuric acid vapors are evolved. Allow the contents of the dish to cool, add 150 ml of water and 3 ml of concentrated hydrochloric acid, boil for 15 minutes, filter, wash completely, and treat the mixture of soluble silicic acid, quartz, and insoluble silicate as on p. 421.

Remark. It was formerly the custom to separate the soluble silica from the insoluble silica by boiling with potassium hydroxide solution. According to the experiments of Lunge and Millberg, however, this is not permissible because quartz is appreciably soluble in caustic potash solution. If, on the other hand, the substance is obtained in a very finely divided condition, even sodium carbonate solution cannot be used, for the same reason.

Analysis of Zircon[2]

Zirconium occurs widely disseminated in small quantities as the refractory silicate zircon, $ZrSiO_4$. In the simple procedure given below, the mineral is decomposed by two successive fusions and the zirconia is precipitated by hydrolysis with thiosulfate. Lundell and Knowles[3] have described a more elaborate process, involving cupferron precipitation, and applicable to more complex mineral mixtures.

Procedure. Reduce the mineral to an impalpable powder, weigh out about 0.5 g in a tared platinum crucible, and heat strongly to determine *loss on ignition.*

Fuse the calcined mass with about 5 g of sodium carbonate in the covered platinum crucible over the full flame of a Teclu burner for an hour. Digest the cooled melt with hot water, filter into a porcelain casserole, and wash the residue well with hot water.   Call this residue A.

To the aqueous extract from the sodium carbonate fusion, add an excess of HCl, evaporate, and dehydrate the silica as described on p. 409. Filter off the silicious residue, and call this B and the filtrate C.

[1] Alexander Subech, *Chem. Ind.*, 1902, 17.
[2] Powell and Schoeller, *Analyst.*, 44, 397 (1919).
[3] *J. Am. Chem. Soc.*, 42, 1439 (1920).

Fuse A with $KHSO_4$ (p. 174), and digest the melt with 100 ml of hot N H_2SO_4. Filter off any undissolved residue, and combine the filtrate with C.

Ignite this last residue together with B in a tared platinum crucible; determine its weight. Treat with H_2SO_4 and HF to determine the SiO_2 present (p. 410). Fuse the residue from this treatment with $KHSO_4$, leach with 1 per cent H_2SO_4, and add the solution to C. After this last fusion, everything except SiO_2 should have been dissolved and be present in C.

Neutralize the acid with $NaHCO_3$ until a slight permanent precipitate is formed. Dissolve this by adding a few drops of dilute H_2SO_4. Add a little ashless filter pulp (p. 151), and saturate the solution with H_2S at 50°. Filter, and wash the precipitate with hot water containing a little NaCl. Discard this precipitate of PtS_2 and S; the purpose of the H_2S treatment was to remove platinum that was introduced into the solution from the crucibles used in the fusions and to reduce the ferric iron to the ferrous condition. Nearly neutralize the filtrate with fresh Na_2CO_3 solution, but stop before there is any permanent darkening due to FeS. Boil in a current of CO_2 to expel H_2S.

To the hot solution add 10 g of $Na_2S_2O_3 \cdot 5H_2O$ dissolved in 20 ml of water and continue boiling for an hour, replacing water lost by evaporation. Add filter-paper pulp (p. 151), filter, and wash the precipitate on a paper filter 15 times with hot water. Call the filtrate D.

The precipitate contains $ZrO_2(HfO_2)$ and possibly some Al_2O_3 and TiO_2. Ignite it in a tared platinum crucible, and digest the oxides with hot N HCl; make ammoniacal and again filter, but wash the residue this time with dilute ammonium nitrate solution (p. 148). Add the filtrate to D. Ignite the residue to constant weight and weigh as $ZrO_2(+ HfO_2$ and possibly a little Al_2O_3 and TiO_2). To determine the Al and Ti in this precipitate, fuse it with 5 to 10 g of Na_2CO_3 for 2 hours in a platinum crucible over a Teclu burner. Leach the melt with hot water, and determine the Al in the filtrate (which contains sodium aluminate) by making acid and proceeding as described on p. 148. Fuse the ignited residue from this last Na_2CO_3 fusion with $KHSO_4$ and determine the Ti colorimetrically (p. 159).

Any iron present in the mineral is contained in the filtrate D. Boil with a little Na_2CO_3 and Br_2, and filter off the precipitate. Dissolve it in dilute HCl, reprecipitate with NH_4OH, ignite, and weigh as Fe_2O_3.

Analysis of Chromite

Although chromite (chrome iron ore) is not a silicate, it is insoluble in all acids, and can be brought into solution by fusion with alkali carbonates, or borates, so that its analysis will be discussed at this place.

Chromite contains 18-39 per cent FeO, 0-18 per cent MgO, 42-64 per cent Cr_2O_3, 0-13 per cent Al_2O_3, and 0-11 per cent SiO_2. Occasionally calcium, manganese, and nickel are present also.

Of the finely powdered and bolted mineral, fuse 0.5 g in an inclined, open platinum crucible with 4 g of pure sodium carbonate[1] for 2 hours over a good Teclu or Méker burner. After cooling, leach the melt with water, acidify with hydrochloric acid,[2] evaporate in a porcelain dish until a dry powder is obtained, moisten with hydrochloric acid, take up in water, and filter off the silica. Ignite, weigh, and test the purity with hydrofluoric acid (p. 410). Introduce hydrogen sulfide into the hot filtrate from the silicic acid and filter off the precipitate of platinum sulfide and sulfur. Catch the filtrate in an Erlenmeyer flask, add 10 ml of ammonium chloride, enough ammonia (free from carbonate) to make the solution alkaline, and a little freshly prepared ammonium sulfide. Stopper the flask and allow the contents to stand over night. In the morning filter off the precipitate, wash twice with water containing a little ammonium sulfide, dissolve it in hydrochloric acid, and repeat the precipitation with ammonium sulfide. Determine calcium and magnesium in the filtrate as described on p. 249.

Dissolve the ammonium sulfide precipitate in cold 2 N hydrochloric acid, filter off any residue of nickel or cobalt sulfide, and dry. Ignite this residue first in air, then in a current of hydrogen, and finally weigh as metal. It is not worth while to attempt the separation of the nickel from the cobalt on account of the small amount present. Expel hydrogen sulfide from the filtrate from the sulfides of nickel and cobalt by boiling, oxidize the iron present by adding bromine, and separate the iron, chromium, and aluminum from the manganese by means of the barium carbonate method (p. 207) and from one another as described on pp. 167 et seq. In the filtrate from the barium carbonate precipitate, separate the manganese from the barium as described on p. 189, b, and determine as sulfide or as sulfate.

Remark. The determination of the chromium alone is best accomplished by means of a volumetric process (see Chapter XV).

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[1] Bunsen fused the chromite with one-third as much SiO_2 and 6-8 parts Na_2CO_3 and then subtracted the amount of silica added from the total amount found. This makes the decomposition take place more readily, but the author prefers not to add the silica on account of the possibility of thereby introducing an error.

[2] If a dark residue of undecomposed mineral should remain, filter it off and again fuse with sodium carbonate.

Determination of Thorium in Monazite Sand[1]

(a) *Separation of Thorium and Cerium by Sodium Thiosulfate*

Monazite is essentially $CePO_4$ with some lanthanum and didymium phosphates usually present. It occurs in so-called "monazite sand" mixed with thoria, quartz, rutile, zirconia, tantalates, etc., and has been used as raw material for the preparation of thoria (used in the Welsbach mantle). The value of a sample of monazite sand depends upon the amount of thorium present, and its determination is best accomplished as follows:

Digest 50 g of monazite sand in a porcelain dish with 100 ml of concentrated sulfuric acid for about 5 hours, or until no yellow, undecomposed grains remain. This treatment easily dissolves all the thoria, which determines the value of the sand but does not dissolve much ilmenite. It is advantageous not to get all the TiO_2 into solution as this will interfere with subsequent work. Cool, and mix slowly with *500 ml of ice-cold water contained in a liter measuring flask. Allow to stand over night.*

In the morning, make up to the mark, mix, and filter. Use 100 ml of the filtrate for the subsequent analysis. If metals of the copper-tin group are present, saturate the solution with hydrogen sulfide, filter, wash, and heat the filtrate to expel the excess hydrogen sulfide. Add NH_4OH and NH_4Cl to precipitate the rare earths with the iron-aluminum group. Filter and wash the precipitate.

Dissolve the precipitate in dilute hydrochloric acid,[2] adjusting the acidity so that approximately 0 1 g of rare-earth oxide is present in 60 ml of solution which is not over 0 5 N in hydrochloric acid. Heat the solution to 60°, and precipitate the rare-earth oxalates by the addition of sufficient oxalic acid to leave about 3 g of the crystals in 100 cc of the final solution. Allow the solution to stand at 60° for some time, preferably over night. (If considerable titanium or zirconium is present, it is best to ignite the precipitated oxalates, dissolve in hydrochloric acid, and repeat the precipitation with oxalic acid.) Filter off the oxalate precipitate; wash thoroughly with hot water containing a little hydrochloric and oxalic acids.

Ignite the rare-earth oxalates to form the oxides. Dissolve the oxides in hot hydrochloric acid, and evaporate the solution to dryness on the water bath. Moisten the residue with 5 ml of water and again dry. Then add 200 ml of water and 9 g of sodium thiosulfate crystals dissolved in 30 ml of water. Allow to stand over night. In the morning, boil the solution for 10 minutes and filter off the precipitate of $Th(OH)_4$ and sulfur. Wash with hot water and boil the filtrate vigorously for an hour to see if there is any further precipitation. If so, filter through a fresh filter, wash thoroughly, and set this precipitate aside.

Wash the main precipitate back into the original beaker with as little water as possible, boil with 10 ml of concentrated hydrochloric acid, and filter into a small evaporating dish, washing the sulfur precipitate well. Evaporate the filtrate to dryness, and repeat the entire treatment with water and sodium thiosulfate, using

[1] U. S. Bur. Mines, *Bull.* 212.

[2] The directions here given originated with Schoeller and Powell, *Analysis of Minerals and Ores of the Rarer Elements, 1919.*

150 ml of water and only 3 g of sodium thiosulfate dissolved in a little water. Finally make a third precipitation in the same way.

Test the filtrates from the second and third thiosulfate precipitations by adding ammonia; if any considerable precipitation takes place the thiosulfate precipitation must be repeated.

Dissolve the final precipitate of thorium hydroxide in 20 ml of 6 N hydrochloric acid, dilute the solution to 150 ml, heat to 60°, and add 30 ml of cold, saturated oxalic acid solution. Allow to stand half an hour, then stir vigorously and allow to stand at least 4 hours at 60°. Filter; wash with hot, very dilute hydrochloric and oxalic acid solution. Ignite the thorium oxalate, and weigh as ThO₂.

Take the precipitate produced by 1 hour's boiling of the filtrate from the first thiosulfate precipitation, the ammonia precipitates after the second and third precipitations, together with the sulfur residues, and ignite. Fuse with potassium pyrosulfate, cool, leach with hot water, precipitate with ammonia, dissolve in hydrochloric acid, evaporate to dryness, and carry out the thiosulfate precipitation as above. Add the small quantity of ThO₂ obtained after the final precipitation as oxalate to that originally obtained.

Notes: 1. The rare-earth oxides rarely dissolve perfectly in hydrochloric acid. When no more seems to dissolve, add a little potassium iodide and reheat. Boil off most of the iodine and oxidize the remainder with a little sulfurous acid and filter until a clear filtrate is obtained.

2. If the initial separation of the rare earths as oxalates has been properly performed so that only traces of phosphate are contained in the precipitate, then if the final thiosulfate precipitate is washed and ignited to oxide it will be only about 0.2 per cent too heavy.

3. When extreme accuracy is not necessary, the filtrate from the first oxalate precipitation and that from the three thiosulfate precipitates can be neglected and the last thiosulfate precipitate ignited and weighed.

(b) Separation of Cerium and Thorium by Potassium Iodate[2]

The thiosulfate method is long and tedious. The iodate method is much more rapid and gives results which are nearly, if not quite, as good.

Treat 50 g of monazite sand with sulfuric acid, as described above, and use one-tenth of the diluted solution. To the 50 ml aliquot, add 50 ml of concentrated nitric acid and cool. Add a solution of 15 g of potassium iodate in 30 ml of water and 50 ml of concentrated nitric acid. Cool and allow to stand half an hour with frequent stirring. Allow the white flocculent precipitate of thorium iodate to settle and filter. Wash the precipitate back into the beaker and cover with 200 ml of a solution containing 8 g of potassium iodate and 200 ml of 6 N nitric acid per liter. Again pour through the filter and use the last solution for washing the precipitate. Rinse off the precipitate with hot water into the beaker again, heat to boiling, and dissolve the precipitate by adding dropwise 30 ml of concentrated nitric acid, or more if necessary. Dilute to 100 ml, cool, and reprecipitate the thorium as iodate by adding 4 g of potassium iodate dissolved in a little concentrated nitric acid and water.

To remove titanium and zirconium, dissolve the precipitate in hydrochloric acid

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[1] These notes were very kindly furnished by H. F. V. Little of Thorium, Ltd., London.

[2] Meyer and Speter, *Chem. Ztg.*, 34, 306 (1910); Schoeller and Powell, *loc. cit.*

and a little sulfurous acid to reduce any cerium to the cerous condition, make slightly basic with ammonia, and filter. Wash the precipitate free from iodide, dissolve again in hydrochloric acid, and precipitate the thorium as oxalate by means of a large excess of oxalic acid as in the preceding method. Ignite and weigh as ThO_2.

Water in Silicates

The total hydrogen of any substance can be determined under suitable conditions as water; Hillebrand[1] has classified the hydrogen that is present in minerals as *essential hydrogen* or *non-essential hydrogen*.

Essential hydrogen represents a characteristic constituent of the mineral and may be present as acidic hydrogen, basic hydrogen, or water of crystallization. Thus the hydrogen of the minerals $KH_2Al_3(SiO_4)_3$, $FeHO_2$, and $Fe_3(PO_4)_2 \cdot 8H_2O$ can be regarded as representing essential hydrogen. Non-essential hydrogen is not necessary for the characterization of the mineral. It may be present in a supercooled solution, it may be held by adsorption or occlusion as water on the walls of cavities or the exteriors of crystals, or it may be included as water in the cavities or grains of minerals.

No rule can be laid down to enable the chemist to differentiate sharply between the different classes.

If the mineral on ignition loses nothing but water, the amount of the water can be determined by the loss in weight. Usually, however, other constituents (e.g., CO_2, SO_2, Cl, F, etc.) are lost, and the substance may undergo an oxidation (FeO is changed to Fe_2O_3; PbS to $PbSO_4$, etc.). In such cases the procedure recommended by Jannasch can be used to advantage. The substance is heated with lead oxide, and the water vapor is conducted over a heated mixture of lead oxide and lead peroxide and absorbed in a weighed calcium chloride tube (see p. 408).

If the substance on ignition loses simply water and carbon dioxide the water may be accurately determined by the method of Brush and Penfield.[2]

Brush and Penfield's Method

The rock powder is heated in a hard glass tube, closed at one end, containing one or more enlargements to provide for the condensation of the water. For most purposes, the tube a shown in Fig 70 is satisfactory. It is 20–25 cm long and has an internal bore of about 6 mm If the water is expelled with difficulty, the tubes b and c are sometimes preferred The tube d is a thistle tube used for introducing the powder into the tube, and e is a tip which is placed on the open end of the tube during the heating to prevent diffusion of air in and out of the tube. At the start

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[1] U. S. Geol. Survey, *Bull.* 700.

[2] *Am. J. Sci.*, [3] 48, 31 (1894), and *Z. anorg. Chem.*, 7, 22 (1894); Washington, *The Chemical Analysis of Rocks.*

and finish, it is important that the tube should be dry on the inside. To dry the tube, insert a piece of glass tubing, extending to the bottom of the tube, and connect the outer end with the suction pump. In weighing the tube, a brass tube support should be used for holding it on the balance pan.

First weigh the tube and its brass support. Then introduce about 1 g of the rock powder through the thistle tube, which must be dry on the inside. A suitable filling tube can be made from a 5-cc pipet,
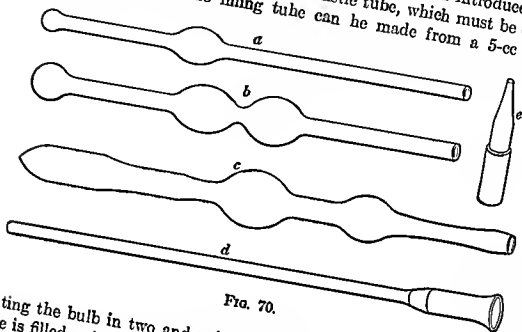
Fig. 70.

cutting the bulb in two and reducing the length to 25 cm. After the tube is filled weigh the tube and brass support again to find the weight of powder taken. Avoid rolling any of the powder toward the open end.

Clamp the tube in a horizontal position, and tap it gently to afford a free passage for the heated air above the powder and connect the tip e with the open end of the tube. Place a narrow strip of filter paper or lamp wicking around the bulb and the farther end of the tube, with the ends dipping in cold water. This is to keep the walls of the tube cold so that water will condense but the wicks should not be so near the open end that there is any chance of water getting into the tube from the outside.

Carefully heat the closed end of the tube, gradually increasing the heat until the full heat of a Tirrill burner is obtained. With some minerals the heat of the Méker burner is necessary. If the end of the tube tends to sink, gently turn it around from time to time.

After the powder has been well ignited, and the water completely expelled, which will take at least 15 minutes, seal a short piece of narrow glass tubing to the hot end of the tube where the substance lies, to serve as a handle. Lower the flame and cautiously drive any condensed moisture near the substance into the bulb, taking care not to

crack the tube. When this is accomplished and there are no longer any drops of water near the substance, soften the hot end by heating with the tip of a Méker burner. When the tube is sufficiently soft all around, draw off the end containing the powder and seal the tube without allowing the flame to enter.

Allow the tube to cool in a horizontal position, wipe dry on the outside, and weigh after it has reached room temperature, removing the tip while weighing. It is well to test the condensed water with litmus to see if it is acid or basic. After the tube has been weighed, dry with suction as at the beginning before the first weighing. Cool, wipe dry on the outside, and weigh again. The difference between the last two weights is the amount of *total* water contained in the rock powder.

If the rock contains minerals like talc, topaz, chondrodite, or staurolite, it is necessary to use a high temperature in the original heating. If constituents like SO_2, S, Cl, or F are present it is necessary to add as retainer a substance such as lime, previously ignited and cooled. Add about 0.2 g through the thistle tube after the rock powder has been weighed.

To correct for the loss of water by evaporation, assume that 0.0003 g of water is lost per hour. If considerable carbon dioxide is present as carbonate in the powder, assume that each gram of CO_2 escaping from the tube will cause the loss of 0.0096 g of water.

Method of Gooch

The tabulated crucible devised by Gooch is useful for the determination of hydrogen (or water) in minerals which require a flux and a high temperature. Mix 0.5 g of the powder with 2.5 g of fully dehydrated sodium carbonate (heated nearly to melting and cooled in a desiccator) in the crucible C, Fig. 71. Place the crucible on a triangle, put the top in place; connect on one side with a calcium chloride tower and soda-lime tubes to free the air from moisture and carbon dioxide and connect on the other side with a sulfuric acid bulb-tube. If it is desired to determine carbon at the same time, use 10 g of fused lead chromate instead of the sodium carbonate as flux. Seal the top of the crucible by pouring powdered sodium tungstate (free from arsenic which would ruin the crucible), or sodium tungstate, into the flanged lip L, immerse the crucible in cold water, and melt the flux in the lip by the flame from a blast lamp. As soon as the flux is fused withdraw the flame and stopper the tubes through which air is passed. When the flux cools, a tight joint is made as shown by the maintenance of the height of sulfuric acid in the bulb-tube as it is sucked back during the contraction of the crucible on cooling.

Dry at 105° for an hour by means of an air or toluene bath while passing dry air through the crucible. Then connect the crucible with a

weigbed calcium chloride tube and the tube witb a weigbed Ascarite bulb (p. 325) if the determination of carbon is to be made also. Shield the sodium tungstate joint from the flame by a horizontal piece of asbestos board and place a similar vertical shield between the crucible and the weigbed absorption tubes. Connect the outer absorption tube with
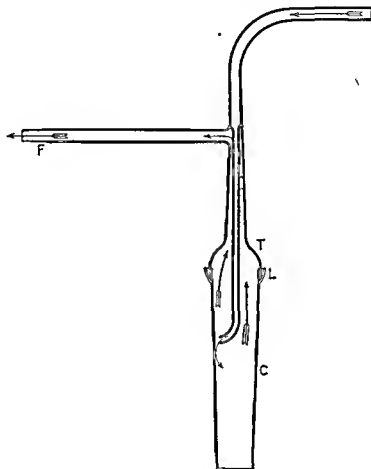
FIG. 71.

the sulfuric acid bulb to show the rate at wbich the gas is passing through the apparatus. Slacken the air stream and carefully heat the crucible witb a free flame, beginning at the top of the rock mixture. When the fusion is complete, as shown by a lessening of the rate at whicb gas escapes, extinguisb the flame and allow a current of air to continue until the apparatus is cold. Only a few minutes are required for the heating. Cool and weigh the absorption bulb with the usual precautions.

Obviously the determination can be made in a glass tube in a sbort combustion furnace.

Analysis of Tantalite or Columbite[1]

Tantalite and columbite are isomorphous orthorhombic minerals containing tantalic and columbic acids in combination with ferrous and manganous oxides: $(Ta, Cb)_2O_5 \cdot (Fe, Mn)O$. Tantalic acid preponderates in tantalite; columbic acid, in columbite. The method given below permits the determination of the essential constituents of the mineral in a sample weighing 0 25 g or less.

Grind the mineral to an impalpable powder, and fuse 0.5 g with 4 g of potassium bisulfate in a silica crucible. Spread the fluid melt so that it solidifies in a thin layer. Cool, and fill the crucible with part of the hot solvent (4 g of tartaric acid in 50 ml of water). When detached, transfer everything to a 400-ml beaker with hot water, rinse the crucible, and add the rest of the solvent. Stir the liquid without interruption until the cake has disintegrated, leaving a pulverulent white residue which dissolves to a clear solution when the liquid is subsequently heated just to boiling during constant agitation. If this residue is allowed to settle, it begins to cake and adhere to the beaker, part of the tantalic acid becoming insoluble; in such a case, filter off and retreat the insoluble fraction, or begin again with a fresh 0.5-g portion.

Treat the liquid with 5 ml of 10 per cent H_2SO_4, and introduce H_2S until it is cold. Stir in a little filter pulp, allow to stand for an hour or two, and collect the precipitate and residue. Wash with acidulated H_2S water; gently ignite in a porcelain crucible, and weigh as SnO_2 *plus* silicious gangue. Determine the tin as on p. 94.

The filtrate contains hydrogen sulfide, and the iron as ferrous salt. Heat it to boiling, add 30 to 35 ml of strong hydrochloric acid, and boil for 2 minutes (cf. Vol. I, p. 588). Allow the white earth-acid precipitate to settle, decant the clear liquid through an 11-cm filter, mix the precipitate with a liberal proportion of filter pulp, and transfer to the filter. With a stream of 0.2 N HCl from a wash bottle, return the precipitate to the beaker, stir up well, again collect on the filter, and finish the washing. Ignite the wet precipitate in the tared silica crucible, and reserve (A).

Evaporate the filtrate from the earth-acid precipitate in a large beaker to small bulk, transfer to a 250-ml beaker, and evaporate to about 20 ml. Reduce the ferric salt with hydrogen sulfide; add a decided excess of strong ammonia and 10 ml of fresh ammonium sulfide solution. The precipitate contains all the iron and all but a few milligrams of the manganese. Allow to stand for 2 hours, collect the precipitate on a 9-cm filter containing a small pad of filter pulp pressed into the apex,

[1] Schoeller and Webb, *Analyst,* 59, 669 (1934).

and wash with water containing ammonium sulfide and chloride. Ignite the precipitate, dissolve it in strong hydrochloric acid, and separate iron from manganese by the basic acetate process (p. 209).

Slightly acidify the filtrate from the sulfide precipitate with acetic acid, boil off hydrogen sulfide, and add a fresh solution of 1 g tannin and 5 g of ammonium acetate. The colored precipitate consists of the small earth-acid fraction not precipitated by hydrolysis with hydrochloric acid. Filter, wash the precipitate with 2 per cent ammonium chloride solution, and ignite in the silica crucible containing the major fraction (A). Leach the ignited precipitate in a small beaker with 0.5 N hydrochloric acid, make slightly ammoniacal, collect the precipitate, ignite strongly, and weigh as $Ta_2O_5 + Cb_2O_5$.[1] For the separation of tantalum from columbium, the precipitate is treated as indicated on p. 224 ("Tannin Methods": No. 4).

The filtrate from the tannin precipitate contains a few milligrams of manganese. It is best to boil it down with a large excess of nitric acid and 5 ml of sulfuric acid for the destruction of the tannin, tartaric acid, and removal of chloride. Dilute the colorless final acid solution with water, and test the liquid colorimetrically with persulfate and silver nitrate (see p. 192).

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[1] It is assumed that the mineral is substantially free from titania.

PART II. VOLUMETRIC (TITRIMETRIC) ANALYSIS

CHAPTER XIII

GENERAL CONSIDERATIONS

The fact that silver chloride is practically insoluble in water furnishes the basis of qualitative tests for both silver and chlorine and for the quantitative determination of both these elements. There are two ways in which this can be done. Thus the weight of the silver chloride precipitate from a known weight of sample furnishes sufficient data for the computation of the percentage of chlorine present. Such an analysis is called *gravimetric* because the computation is based upon weights. The second way of carrying out the analysis is to measure the volume of silver nitrate solution required to precipitate completely all the chloride present. Then, if the concentration of the silver nitrate solution is known, the chlorine content can be computed. This is called *volumetric* analysis because the result is obtained by measuring a volume. The process of determining the volume of reagent required to bring a definite reaction to completion is called titration. Many prefer, therefore, to call this *titrimetric analysis*. This term is less ambiguous because in gas analysis *volumes* are measured. For volumetric or titrimetric analysis, accurately calibrated measuring instruments are necessary.

Measuring Instruments

1. *Burets* are tubes of uniform bore throughout the entire length; they are graduated in milliliters[1] and are closed at the bottom, as shown in Fig. 72, by means of a glass stopcock, or with a piece of rubber tubing containing a glass bead h. The latter form was devised by Bunsen and is used as follows: Seize the tubing between the thumb and forefinger

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[1] The liter as defined by the National Bureau of Standards represents a volume of 1000 027 cubic centimeters. The one-thousandth part of a liter is called the milliliter, abbreviated mL. It is almost but not quite the same as a cubic centimeter, or cc.

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at the place where the glass bead is, and, by means of gentle pressure at the top of the bead, form a canal at one side of the bead through which the liquid will run out. Instead of the glass bead an ordinary pinch-cock is sometimes used.

Besides the above forms of burets, many others are in use, but it is unnecessary to describe them here.

2. *Pipets.* A distinction must be made between a *transfer* pipet and a *measuring* one. A transfer pipet has only one mark upon it, and serves for measuring off a definite amount of liquid. Transfer pipets are constructed in different forms; usually they consist of a glass tube with a cylindrical widening at the middle. The lower end is drawn out, leaving an opening about 0.5–1 mm wide. Pipets of this nature are constructed which will deliver respectively 1, 2, 5, 10, 20, 25, 50, 100, and 200 ml. For delivering these definite volumes of liquid, pipets are more accurate than burets or flasks.

Fig. 72.

Measuring pipets are buret-shaped tubes graduated in milliliters and drawn out at the lower end. They serve to measure out any desired amount of liquid and are obtainable with a total capacity of 1, 2, 5, 10, 20, 25, and 50 ml.

3. *Measuring flasks* are flat-bottomed flasks with narrow necks provided with a mark, so that when they are filled to this point they will contain respectively 50, 100, 200, 250, 300, 500, 1000, and 2000 ml. They serve for the preparation of standard solutions and for the dilution of fluids to a definite volume.

4. *Measuring cylinders* are graduated in milliliters and are used only for rough measurements.

It is clear that accurate results can be obtained by a volumetric analysis only when the instruments used are accurately calibrated. It should never be taken for granted that a purchased instrument is correct, but it should always be tested carefully.
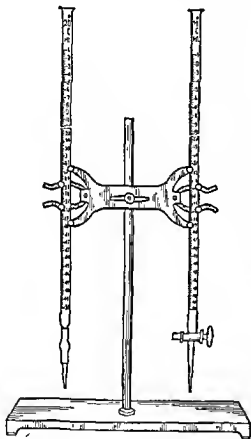
Normal Volume and Normal Temperature

A liter, which is the volume of a kilogram of water at its maximum density, is taken as the normal volume. If it is desired to mark on the neck of a liter flask the point to which this volume reaches, the position of the mark depends upon the temperature of the vessel. It is necessary, therefore, to choose for the vessel itself a definite temperature, the so-called *normal temperature*. At present the temperature of $+20°C$ is taken as the normal temperature by the National Bureau of Standards. According to this, then, the flask should contain at 20° the volume that would be occupied by a kilogram of water at $+4°$, and as the kilogram is the unit of mass, the weighing should also take place in a vacuum.

The following table gives the density, or weight of 1 ml of water in a vacuum, at different temperatures.

DENSITY OF WATER AT DIFFERENT TEMPERATURES

t	Density	t	Density	t	Density
0°	0 999867	14°	0.999271	28°	0 996258
1	9926	15	9126	29	0.995069
2	9968	16	8969	30	5672
8	9992	17	8801	31	5366
4	1 000000	18	8621	32	5052
5	0.999992	19	8430	33	0.994728
6	9968	20	8229	34	4397
7	9929	21	8017	35	4058
8	9876	22	0 997795	36	0.993711
9	9808	23	7563	37	3356
10	9727	24	7321	38	0 992993
11	9632	25	7069	39	2622
12	9524	26	0.996808	40	0.992244
13	9404	27	6538		

It is experimentally impossible to weigh water at 4° in a glass vessel at 20° and in a vacuum, but with the aid of (1) the above table, (2) the known expansion of glass with rise in temperature, and (3) the buoyancies of water and of brass when surrounded by air, it is possible to calculate what the weight of 1 l of water is when weighed in the air at any temperature from 1° to 40°. The weights which must be placed upon the balance pan in order to determine the space occupied by a true liter of water, therefore, depend upon the temperature of the water and of the vessel, as well as the density of the air at the time of the experiment. The density of the air varies somewhat from day to day, depend-

ing upon the barometric pressure, the temperature, and the humidity. It usually suffices, however, to assume the average values of these factors, and in this way the following table has been computed to show the apparent weight in air with brass weights for temperatures between 15° and 30° under 50 per cent humidity and at a barometer reading of 760 mm.

If the glass vessel is at 20° no other correction is necessary. The glass, however, expands with rise of temperature. The coefficient of cubical expansion[1] varies from 0.000023 to 0.000028 per degree C. An average value of 0.000025 can be assumed.

APPARENT WEIGHT IN GRAMS OF WATER IN AIR

Temp. in Degrees C	2000 ml	1000 ml	500 ml	400 ml	300 ml	250 ml	150 ml
15	1996.11	998.05	499.03	399.22	299.42	249.52	149.71
16	1995.80	997.90	498.95	399.10	299.37	249.48	149.68
17	1995.48	997.74	498.87	399.10	299.32	249.43	149.66
18	1995.13	997.56	498.78	399.03	299.27	249.39	149.63
19	1994.76	997.38	498.69	398 95	299.21	249.34	149.61
20	1994.36	997.18	498.59	398 87	299.15	249.30	149.58
21	1993.95	996.97	498.49	398.79	299.09	249.24	149.55
22	1993.51	996.76	498.38	398.70	299.03	249.19	149 51
23	1993.00	996.53	498.26	398.61	298.96	249 13	149.48
24	1992.58	996.29	498.15	398 52	298.89	249.07	149.44
25	1992.09	996 04	498.02	398.42	298.81	249.01	149.41
26	1991.57	995.79	497.89	398 31	298.74	248.95	149.37
27	1991.04	995.52	497.76	398.21	298.66	248 88	149.33
28	1990.49	995.24	497.62	398.10	298.57	248.81	149 29
29	1989.92	994.96	497.48	397.98	298.49	248.74	149 24
30	1989 33	994.66	497.33	397.87	298.40	248.67	149.20

The expansion of water from 4° upward makes the weight of 1 liter of water smaller, and, since water is less dense than the weights, weights of water in the air will always be less than they would be in a vacuum. If the temperature of the glass container is above 20°, the volume will be a little larger than it would be at 20°, which corresponds to greater weight, but this gain in weight is small compared with corrections caused by the expansion of water and by the buoyancy of the air so that, at the laboratory temperatures, the weight in grams is invariably

[1] At first sight it may seem strange to consider the cubical expansion of glass in calibrating. If, however, we consider a cube of glass with a cavity cut in it of 10-cm edge, then on heating it the cavity will expand to the same extent as if the glass had not been cut out. We measure, therefore, the cubic expansion of glass which has been removed in order to find the change in volume of a glass measuring vessel.

a little smaller than the volume in milliliters. In the above table the weight in air of exactly the specified volumes of water is given. The table does not take into consideration the fact that the measuring vessel expands and if it reads correctly at 20° it will contain somewhat less at lower temperatures and somewhat more at higher temperatures. Thus a glass volumetric flask which holds exactly 1000.00 ml at 20° will hold 1000.25 ml at 30°, and this quantity of water will weigh 994.92 g in the air instead of 994.66 g as given in the table. The difference between the weight 994.92 and the volume 1000 ml is 5.08, and, when the flask is calibrated correctly within 1 ml of the specified volume, we can get the exact volume, within 0.01 ml, by adding the value 5.08 to the weight of the water when the temperature is 30°.

The following table is convenient for testing glass apparatus which is calibrated with the precision to be expected when purchased from reputable dealers. It gives values to add to the weight of the water in grams to get the number of milliliters which the glass measuring vessel indicates at 20°.

VOLUME OF ONE LITER FROM THE WEIGHT OF WATER IN AIR

Temp.	Add	Temp.	Add	Temp.	Add	Temp.	Add
15°	2 07	19 0	2 65	23 0	3 40	27 0	4.31
15 5	2 13	19 5	2 73	23 5	3 50	27.5	4.43
16 0	2 20	20 0	2 82	24 0	3 61	28 0	4 56
16 5	2 27	20 5	2 91	24 5	3 72	28 5	4 69
17 0	2 34	21 0	3 00	25 0	3 83	29 0	4 82
17 5	2 41	21 5	3 10	25 5	3 95	29 5	4.95
18 0	2 49	22 0	3 19	26 0	4 06	30 0	5.08
18 5	2 57	22 5	3 29	26 5	4 18		

This table can be used also for testing other volumes such as that of a 500-ml flask, a 100-ml flask, or a 50-ml pipet, when the proportionate fraction of the above values is taken. Thus in testing a buret by weighing 10-ml portions, add the above values in centigrams to the weight in grams, and the sum will show the volume in milliliters.

Calibration of a Buret

A buret will not drain properly unless it is clean on the inside so that small drops of liquid do not adhere to the sides when the liquid is withdrawn. "Cleaning solution" made from potassium dichromate and concentrated sulfuric acid is efficient for cleaning burets and other glass

apparatus. Dissolve 2 g of **potassium dichromate** in 5 ml of water, heating until all the salt has dissolved, cool the solution, and add slowly, while stirring, about 65 ml of concentrated sulfuric acid.[1] Considerable heat is evolved on the addition of the acid to the water. Fill the buret with the hot chromic acid solution, and allow it to stand 15 minutes or longer. Since this cleaning solution attacks rubber, it is best to remove the rubber tubing from the end of a Mohr or plain buret and force the end into a medium-sized cork stopper. Place a beaker under the buret while it is standing with the cleaning solution in it.

After 15 minutes, let the solution run out and rinse the buret at least four times with water. Then test to see if water drains freely without leaving drops adhering to the sides; if not, the cleaning process must be repeated. The cleaning solution can be kept and used repeatedly. It should be warm but not boiling hot when being used. Before pouring the used cleaning solution down the sink, remember to start the water running freely so that the acid will be largely diluted and will not attack the piping.

Remove the stopcock of the glass-stoppered or Geissler buret, wipe it dry, and also wipe the inside of the ground joint in the buret. Smear the surface with stopcock lubricant,[2] and replace in the buret. Fasten the stopcock in place with some No. 24 copper wire.

Fill the buret with distilled water, making sure that the water extends to the very tip of the stopper with no air bubble there. To remove the air from a plain buret, raise the tip so that it is above the bottom of the glass cylinder and allow water to run out from the upturned tip; the lighter air tends to flow upward. The buret is now ready to be calibrated. Drain out water so that the upper level is close to the zero mark.

Weigh a 50-ml, flat-bottomed, narrow-necked flask to the nearest centigram. The outside of the flask must be dry, but it is not necessary to have the inside dry or cleaned with chromic acid solution. It is a waste of time to read the weight closer than to the nearest centigram, because one cannot read the buret closer than to the nearest 0.01 ml,

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[1] Cleaning solution containing 15 g $K_2Cr_2O_7$ or $Na_2Cr_2O_7$ in 500 ml of concentrated sulfuric acid is efficient for cleaning glassware. It should be kept in a glass-stoppered bottle and handled with care as it makes holes in clothing If spilled it should be diluted with water and neutralized before being sponged up. Spilled concentrated acid should never be allowed to remain unneutralized on the floor or working bench.

[2] Vaseline can be used as lubricant but is a little thin. *Lubriseal*, sold by the A. H. Thomas Co. of Philadelphia, is better. A good lubricant can be made by melting together, on the water bath, 16 parts of Vaseline, 8 parts of pure gum rubber, and 1 part of paraffin.

and rapid weighing is advantageous to avoid error due to evaporation. Record the weight in the notebook. (See p. 440.)

Read the buret to the nearest 0.01 ml, and record the reading. Check each weight and each reading after setting them down in the notebook. In reading the buret, it is best to read the bottom of the meniscus, except with dark-colored liquids like potassium permanganate solution, in which case the top of the meniscus should be read. It is important that the eye should be directly opposite to the point read. If the eye is above the meniscus, the reading will be too high, and if the eye is too low the reading will be low. To avoid such parallax errors, the Bureau of Standards has asked the makers of burets to make the lines complete circles; the position of the eye is correct when the circle nearest to the bottom of the meniscus appears to be a straight line. When all the lines are circles, it is a little confusing to some eyes, so that many chemists prefer to use burets in which the lines of graduation do not extend very far and with lines of different lengths so that one can readily distinguish the whole and half milliliter lines. In such cases, it is well to take a strip of blue glazed paper with a straight and smooth edge. Wrap this strip around the buret evenly, with the colored edge on the inside. If the paper is placed about two divisions below the bottom of the meniscus, the eye will be level when the inside blue of the paper just comes into view. The blue also serves to make the tip of the meniscus appear a little darker and more sharply defined. With a little practice, one can easily learn to estimate the exact position of the meniscus within 0.01 ml.

After reading the buret, drain out 10 ml of water into the weighed flask, stopping as closely as possible to the 10.00 mark but not wasting much time trying to get it exactly there because there will be a slight drainage while the weighing is being made.

Then, without stopping to make an exact reading of the buret, weigh the flask and its contents to the nearest centigram. After this read the buret and allow water to run into the flask until the 20.00 mark is reached, continuing in this way until the buret has been drained to the lowest calibration mark. Record the weighings in the notebook according to the plan on p. 440.

When the calibration is finished, fill the buret again and repeat the work. In the second testing the corrections for each 10 ml should check with the first within 0.02 ml. From the average values, make a plot using one division of vertical distance on the paper to represent 1 ml of buret reading and each division of horizontal distance to represent 0.01 ml of correction. Then, on the plot, the total distance from the base line will show the correction to be applied for any given reading

BURET CALIBRATION. TEMPERATURE 25°

Weights	Difference	Buret Readings	Difference	True Volume* of Each Portion	Correction for 10 ml	Total Correction
20.52		0.01				
30 50	9.98	9.96	9.95	10.02	+.07	+.07
40.52	10.02	19.95	9.99	10.06	+.07	+.14
50.47	9.95	29.93	9.98	9 99	+.01	+.15
60.39	9 92	39.91	9.98	9.96	−.02	+.13
70.40	10.01	49.85	9.94	10.05	+.11	+.24

* The table on p. 437 shows that the correction to be added to the weight of 1 l of water when weighed in the air at 25° is 3 83 g For 10 ml (1/100 liter) the correction will be 0 0383 g. Since the buret cannot be read to less than 0 01 ml, the correction used is 0 01 g. For very accurate work, weight burets are used in which the stoppered buret is weighed at the start and finish of each analysis. With such a buret the analysis can be made more accurately; see p. 446.

of the buret. Many burets are obtained today which are calibrated so accurately that there is no need for applying buret corrections, particularly if one always makes a practice of beginning at about the zero mark with every standardization and in every analysis. It is not safe, however, to assume that a buret is correct without testing it.

Instead of calibrating the buret in the manner just described, many chemists prefer to start each time at the zero point, refilling the buret after each withdrawal of 10, 20, 30, or 40 ml of liquid. Others prefer to calibrate by causing the water to flow through a carefully calibrated small pipet, reading the buret after each withdrawal of a pipetful of water.

Calibration of a Buret with a Calibrating Pipet

Clean the calibrating pipet, P, in Fig. 73, with cleaning solution, and attach it to the tip of the cleaned buret and to another glass stopcock, S_2. The connections at A and B should be made by pressing the glass ends into thick-walled rubber tubing until the glass edges of the buret tip and of the pipet side arm make a glass-to-glass connection. Clamp the buret and the pipet rigidly in position (the clamps are not shown in the drawing). Fill the entire apparatus, from above the zero mark of the buret to the tip of stopcock S_2, with distilled water at room temperature. Manipulate the two stopcocks S_1 and S_2 until the meniscus stands exactly at the zero mark in the buret and at the upper mark C in the pipet. Take care to dislodge all air bubbles. Place a weighed, 50-ml, narrow-necked flask, which has been weighed to the nearest 0.01 g, underneath stopcock S_2, open this stopcock, and care-

fully draw off water until the meniscus is at the mark D; during this operation stopcock S_1 is kept closed.

Now carefully open opcock S_1 of the bsturet and allow water to flow from the buret to the pipet until the meniscus just reaches the upper mark C in the pipet. Close stopcock S_1 and read the bottom of the meniscus in the buret to the nearest 0.01 ml; record this reading in the notebook. Repeat these operations of draining the water down to the mark D in the pipet, filling from the buret to the point C, and recording the buret reading in the notebook until, after 10 withdrawals, the buret reading is close to the 50-ml calibration mark.

Weigh the flask and its contents, and take the temperature of the water. To illustrate the calculations, assume that the temperature was 25° and that the weight in air of the total quantity of water drawn off was 49.62 g. From the table on p. 437 we find that the difference between the weight in grams and the volume in milliliters is 3.83 for 1 l. For 50 ml it is $3.83/20 = 0.19$. The actual volume of water drawn off is, therefore, $49.62 + 0.19 = 49.81$, and each pipetful represents 4.98 ml. The data can be tabulated as follows:
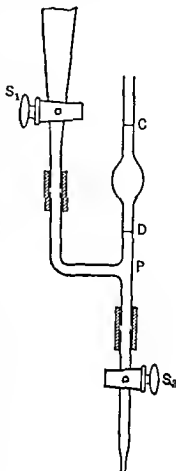
Fig. 73.

Reading No.	Buret Reading	True Volume	Correction	Corrected Reading for each 5 ml
1	0.00	0.00	0.00	0.00
2	4.94	4.98	+0.04	5.04
3	9.96	9.96	0.00	10.00
4	14.91	14 94	+0 03	15.03
5	19.86	19.92	+0.06	20.06
6	24 82	24 90	+0 08	25.08
7	29.83	29.88	+0.05	30.05
8	34.84	34.86	+0.02	35.02
9	39.82	39.84	+0.02	40.02
10	44.83	44.82	−0.01	44.99
11	49.85	49.80	−0.05	49.95

Calibration of a Pipet

Clean the pipet with cleaning solution, but take care not to suck any of the chromic acid into the mouth. To avoid this, attach a piece of rubber tubing to the pipet and apply suction through this tubing. Rinse out the pipet with water. Suck up distilled water to a point above the graduation mark, quickly place the forefinger over the top of the tube, and allow the level of the water to fall until the bottom of the meniscus coincides with the graduation mark. Then allow the contents of the pipet to run into a weighed flask; hold the pipet in a vertical position all the time. As soon as the pipet is empty, touch the tip to the inside surface of the flask and withdraw it. Do not wait for another drop to form and do not blow into the pipet. From the weight of the water, determine the volume of the pipet as in the calibration of a buret.

Calibration of a Flask

Flasks are sometimes calibrated both for content and for delivery. To test the calibration for delivery, clean and weigh the delivered water exactly the same as for burets and pipets.

To test the calibration for content: Clean carefully and dry the flask both inside and outside. Allow it to come to room temperature and weigh the empty flask. Then fill with water up to the mark and weigh again.

To calibrate an unmarked flask, preferably one having a narrow neck, clean, dry, and weigh (or tare[1] carefully). Then place the proper weight on the balance pan and add water until equilibrium is again restored. Note the place on the neck where the bottom of the meniscus comes.

Place the flask upon a level surface and fasten a piece of gummed paper with a straight edge around the neck of the flask so that its upper edge is just tangent to the deepest point of the water meniscus. Empty the flask, dry, cover its neck with a uniform layer of beeswax, and allow to cool; this usually requires about 15 minutes. Then hold the flask, as is shown in Fig. 74, against the piece of wood *s*, place the blade of a pocket knife firmly against the upper edge of the thick paper ring, and revolve the flask through 360° around its horizontal axis; in this way a circle is cut in the wax layer. By means of a feather place a drop of hydrofluoric acid[2] along this circle while holding the flask in the hori-

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[1] The word *tare* is used to represent a counterpoise which may or may not be weights. If weights are used, it is not necessary to record the values.

[2] Hydrofluoric acid produces painful burns. If any of the acid gets on the fingers, wash them well with water *at once*. The acid does not smart, or sting, at first because it has anesthetic properties.

zontal position. By turning the flask around its axis, allow the drop of hydrofluoric acid to act upon the glass where the wax coating has been cut. After 2 minutes wash the excess of hydrofluoric acid off, dry the neck of the flask by means of filter paper, heat until the wax melts,
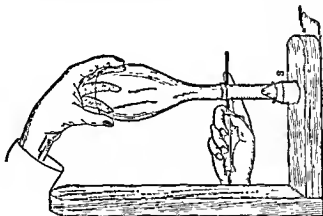
Fig. 74.

and wipe it off. Remove the last traces of wax by rubbing with a cloth wet with alcohol.

If flasks or burets are to be tested in large numbers it is better to use a volumetric method. Thus for testing flasks at the Bureau of Standards a series of volumetric standards has been made up, each standard having a capacity slightly less than that of the flask it is intended to test. When the water from the appropriate standard is delivered into a flask, the flask is filled nearly to the graduation mark. The filling is then completed by means of a finely graduated buret. The capacity of the flask is found from the known volume delivered by the standard and the additional volume delivered by the buret. The flask standard and the buret are themselves calibrated by weighing the water delivered.

For the same purpose, Morse and Blalock devised a set of standard bulbs as shown in Fig 75. In calibrating these bulbs it is necessary to determine, with the aid of the table on p. 437, the capacity from the single mark to the first stem division and the capacity of the stem for the smallest subdivision.

In using this Morse-Blalock apparatus it is not necessary to pay any attention to the temperature after the calibration is once made because, if the temperature of the water is constant during the work, the volume of the flask or buret will correspond to that of the calibrating vessel.

To calibrate a standard bulb, first clean it with soapy water and then with chrome–sulfuric mixture as described on p. 437. Place the bulb so

that the graduated stem is at the bottom as shown in Fig. 76. Use a glass stopcock for controlling the outflow, and the tip of the outflow must he restricted so that the outflow is not over 50 ml per minute. Fill the bulb to the upper mark. With the stopcock wide open allow water to flow into a weighed flask until the first division (zero) is reached. Stopper the flask and weigh. With the aid of the table on p. 437 compute the volume of water and capacity of the bulb. Adjust the liquid again to the zero mark, place a smaller weighed flask
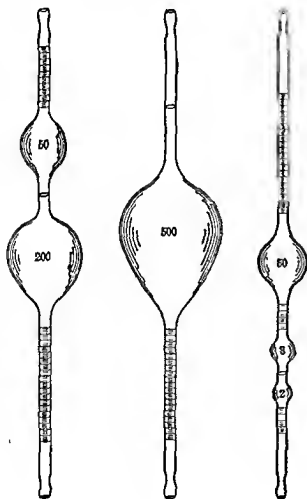
Fig. 75.   Fig. 76.

under the delivery tube, and allow the stem to drain from the zero mark down to the bottom mark. Weigh and compute the volume of each scale division with the aid of the data given in the tables. From these data compute the proper mark on the stem to which the water

should fall in order to make the apparatus deliver the desired volume of water and check this by trial.

For a more accurate calibration of the buret, 2-ml portions may be withdrawn or, by means of the standard tube shown in Fig. 76, the value of each milliliter or any fraction may be determined.

To calibrate a buret, set up the apparatus as shown in Fig. 77. The reservoir must be higher than the top of the buret, and this, in turn, must be placed so that the lowest graduation is higher than the bulbs. With the three-way cock b closed, open the cock a and fill the buret with water. Close a and open b so that the 2-ml and 3-ml bulbs can fill,
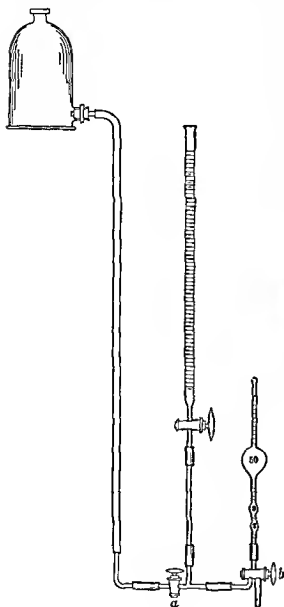
Fig. 77.
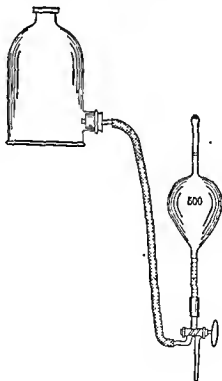
Fig. 78.

then drain the buret to the zero mark and the bulbs to that mark on the stem of the 2-ml bulb which represents exactly 2 ml. This leaves the bulbs properly moistened. Leave the buret cock open. Turn cock b and measure 5 ml of water from the buret into the small

bulbs. Observe the position of the meniscus upon the stem of the 3-ml bulb and calculate the true capacity of the first portion of the buret from the values of the stem divisions as determined in the calibration of the bulbs.

To calibrate a flask, place the flask under the delivery tube and allow water to run into it from the Morse-Blalock bulb (Fig. 78) until the proper mark on the stem is reached and mark the position of the water in the neck as described on p. 442.

For very accurate work, *weight* burets are desirable (Fig. 79). These are stoppered and weighed after each titration. It is possible to weigh a solution more accurately than to read its volume, but as a rule the end point is not accurate enough to warrant this extra bother of weighing.
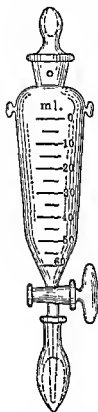
Fig. 79

Concentration of Solutions. Calculations of Volumetric Analysis

Volumetric analysis is based upon the measurement of volumes, but it is necessary to know the strength of the reagent used to accomplish a given reaction. The strength of a solution is determined by its *concentration* or the quantity of reagent in a given volume. A solution of silver nitrate reagent may be prepared by dissolving 25 g of solid silver nitrate in water and diluting the solution to 1 l. The concentration of the well-mixed solution can be expressed by saying that it contains 25 g of silver nitrate per liter, or 25 mg per ml. This method of expressing concentrations in *weight per unit volume* is a very common one. Sometimes the concentration is expressed in weight of solute per unit weight of solvent. Thus, the silver nitrate solution just referred to will contain 25 g silver nitrate in 997.2 g of water at 20°.

In expressing the concentration of aqueous solutions of gaseous substances such as NH_3 or HCl it is common practice to say that the solution contains a certain *percentage by weight*. Thus the table at the back of the hook shows that hydrochloric acid of 1.2 density contains 39.11 per cent HCl by weight. This means that 1 ml of the HCl solution weighs 1.2 g and contains 1.2×0.3911 g of dissolved HCl. In this particular case, the table gives the values on a vacuum hasis.

Sometimes mixtures of two liquids are said to contain a certain *percentage by volume* of one of them. Thus, if 25 ml of pure alcohol is

diluted with water to make 100 ml of solution, the mixture can be said to contain 25 per cent of alcohol by volume.

The physical chemist usually finds it convenient to express concentrations in *moles per liter*, the designation *mole* (German *mol*) meaning a molecular weight in grams. A solution containing 36.46 g of HCl per liter is called, therefore, a *molar* solution.[1] This designation is also applied to ions in solution; a solution is said to be molar in hydrogen ions if it contains 1.008 g of H^+ per liter.

Sometimes the molecular weight of a substance may be in doubt. Thus one chemist may write the formula of mercurous chloride as HgCl and another chemist may prefer Hg_2Cl_2. To avoid misunderstanding of this nature, some chemists make use of the term *formal solution* to represent one formula weight in grams per liter and give the formula of the substance.

There are other ways in which concentrations can be expressed using other units of mass and of volume. Thus the mass can be expressed in grains, ounces, pounds, or tons and the volume in pints, quarts, gallons, or cubic feet.

The value of 1 ml of solution in terms of any substance with which it reacts is often called the *titer* of the solution. This is another way of expressing concentrations.

For the purposes of volumetric analysis none of the above methods of expressing concentration is entirely satisfactory. If we say that 1 ml of HCl solution contains 0.4693 g of dissolved HCl, it is a rather tedious problem in mental arithmetic to decide exactly how much NaOH it will neutralize. It involves the knowledge of the molecular weights of HCl (36.46) and NaOH (40.01). We can carry out such a computation and find, for example, that 1 ml of the HCl solution will neutralize $0.4693 \times 40.01 \div 36.46 = 0.5151$ g of NaOH. This value expresses the concentration of the acid solution in terms of NaOH and is helpful if the acid is to be used for the sole purpose of analyzing samples of NaOH. Another computation is necessary to find out the strength of the solution with respect to any other substance with which it will react.

The most convenient method, however, of expressing the concentrations of solutions for the purposes of volumetric analysis is with reference to equivalent weights.

[1] A solution containing one mole in 1000 g of solvent is often called a *molal* solution. This distinction between a *molar* and a *molal* solution is emphasized by some and disregarded by other chemists.

Normal Solutions

By a *normal solution* is understood one which contains *1 gram equivalent* of the active reagent dissolved in 1 l of solution.[1] By *gram equivalent* is meant the amount of substance equivalent to 1 gram atom (1.008 g) of hydrogen. One milliliter of a normal solution contains one *milliequivalent* of active reagent. For convenience in computation the concentrations of solutions used for volumetric purposes are expressed in terms of their normality; that is, a solution is 2 normal, 0.5 normal, 0.1 normal, etc. The letter N is used as an abbreviation for *normal*.

The gram equivalent, or weight required to make a liter of normal solution, depends upon the nature of the reaction involved. It often happens that the same solution has a certain normal concentration when used for one purpose and a different normal concentration when used for another purpose. The reagents used in volumetric analysis are acids, bases, oxidizing agents, reducing agents, and precipitants.

The equivalent weight of an acid is determined by the number of replaceable hydrogen atoms in the acid molecule. Thus, to make a normal solution of the monobasic hydrochloric, hydrobromic, hydriodic, nitric, or acetic acids, it is necessary to have a molecular weight in grams (*1 mole*) of the acid dissolved in a liter of solution. To make 1 liter of normal solution of the dibasic sulfuric acid only ½ mole of the acid is necessary.

Sometimes, however, it is not convenient to react with all the replaceable hydrogen atoms of an acid. In fact some acids are so weak that they cannot be used in volumetric analysis. Carbonic acid, for example, has no appreciable effect upon methyl orange, and only 1 of the 2 hydrogen atoms in H_2CO_3 is acid toward phenolphthalein.

Phosphoric acid, H_3PO_4, really has 3 replaceable hydrogens, but only the first is acid toward methyl orange and 2 hydrogen atoms are acid toward phenolphthalein. In titrating with methyl orange as indicator, phosphoric acid acts as a monobasic acid and the normal solution contains 1 mole per liter. With phenolphthalein as indicator, phosphoric acid acts as a dibasic acid and ½ mole per liter will make a normal solution of phosphoric acid.

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[1] It is important to note that a normal solution is not properly defined as one containing a gram equivalent in 1 l of *solvent*. In volumetric analysis the unit is always referred to the volume of the solution. The *gram equivalent* will often be referred to as the *equivalent weight* of a substance. The equivalent weight will always refer to 1 l of solution and the milliequivalent to 1 ml.

A normal solution of a base will contain 1 mole of replaceable hydroxide per liter. Thus of potassium hydroxide, KOH, sodium hydroxide, NaOH, and ammonium hydroxide, NH_4OH, 1 mole per liter makes a normal solution. Of barium hydroxide, $Ba(OH)_2$, calcium hydroxide, $Ca(OH)_2$, and strontium hydroxide, $Sr(OH)_2$, only $\frac{1}{2}$ mole per liter is required. Magnesium hydroxide is not appreciably soluble in water, but it is convenient to use the conception of normal solution to determine how much will be dissolved by an acid solution of known strength. One liter of normal hydrochloric acid will dissolve $\frac{1}{2}$ mole of $Mg(OH)_2$.

Salts of weak acids and strong bases have a basic reaction. With methyl orange as indicator, 1 mole of sodium carbonate reacts with 2 moles of hydrochloric acid; hence, the equivalent weight is $\frac{1}{2}$ mole of sodium carbonate. With phenolphthalein, however, the end point is reached when 1 mole of sodium carbonate has reacted with 1 mole of hydrochloric acid; in this case the normal solution will contain 1 mole of sodium carbonate per liter. One molecule of borax, $Na_2B_4O_7$, reacts with 2 molecules of hydrochloric acid when methyl orange is the indicator. If, after this neutralization, considerable glycerol, $C_3H_5(OH)_3$, or some mannitol, $C_6H_8(OH)_6$, is added, one molecule of sodium hydroxide is required for each atom of boron in order to make the solution neutral to phenolphthalein.

The equivalent weight of an oxidizing agent is determined by the change in polarity which the reduced element experiences. The polarity of an element is the sum of the positive and negative valence bonds which it has in a compound; it represents the state of oxidation. Usually the polarity is the same as the valence except that a positive or negative sign is prefixed, but sometimes, as is true of the nitrogen atom of an ammonium salt, there is a difference. Nitrogen in the ammonium radical has a valence of 5, but four of the bonds are negative toward hydrogen atoms and the fifth bond is positive toward the acid ion of the ammonium salt. The polarity of nitrogen in an ammonium salt is −3 and it corresponds to the same state of oxidation as ammonia, NH_3.

When potassium permanganate is used as an oxidizing agent, the manganese drops to a lower polarity. In permanganate the polarity of the manganese atom is +7, and, in most reactions used in volumetric analysis, the manganese is reduced to manganous salt in which the manganese has a polarity of +2:

$$MnO_4^- + 5Fe^{++} + 8H^+ \rightarrow Mn^{++} + 5Fe^{+++} + 4H_2O$$
$$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{++} + 5I_2 + 8H_2O$$
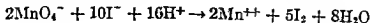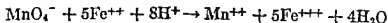
A normal solution of potassium permanganate, therefore, will contain $\frac{1}{5}$ mole of $KMnO_4$ because the atom of manganese loses 5 positive charges in changing from a polarity of $+7$ to $+2$.

Sometimes, however, the manganese of potassium permanganate is reduced only to the quadrivalent state. Thus a hot, nearly neutral solution of a manganous salt can be made to react with permanganate as follows:

$$2MnO_4^- + 3Mn^{++} + 2H_2O \rightarrow 5MnO_2 + 4H^+$$
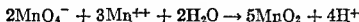
In this case the manganese atom in permanganate loses only 3 charges and, strictly speaking, a normal solution of permanganate should contain only $\frac{1}{3}$ mole of the reagent, but permanganate is usually standardized by a reaction in which it is reduced to manganous salt. *Throughout this book, therefore, a normal solution of permanganate will refer to one containing $\frac{1}{5}$ mole of $KMnO_4$ per liter, and $2MnO_4^-$ will be regarded as 10 equivalents.*

Potassium dichromate is often used as an oxidizing agent. In it each chromium atom has a polarity of $+6$, and by reduction 2 trivalent chromic ions are formed. There is a loss in polarity of 3 charges for each chromium atom, and a normal solution of potassium dichromate, $K_2Cr_2O_7$, will contain $\frac{1}{6}$ mole.[1]

$$Cr_2O_7^- + 6Fe^{++} + 14H^+ \rightarrow 2Cr^{+++} + 6Fe^{+++} + 7H_2O$$
$$Cr_2O_7^- + 6I^- + 14H^+ \rightarrow 2Cr^{+++} + 3I_2 + 7H_2O$$
$$Cr_2O_7^- + 3Sn^{++} + 14H^+ \rightarrow 2Cr^{+++} + 3Sn^{++++} + 7H_2O$$
$$Cr_2O_7^- + 3H_2S + 8H^+ \rightarrow 2Cr^{+++} + 3S + 7H_2O$$
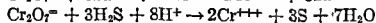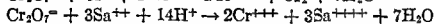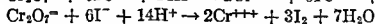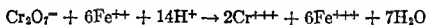
A solution of a ferric salt is sometimes used as a mild oxidizing agent. Thus, it will oxidize the iodide anion

$$2Fe^{+++} + 2I^- = 2Fe^{++} + I_2$$
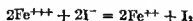
In this case, the oxidation depends upon the reduction of the ferric ion to the ferrous condition, and the equivalent weight of a ferric salt is the molecular weight divided by the number of Fe atoms in the molecule of the ferric salt.

Solutions of ceric salts have been highly recommended for replacing potassium dichromate and potassium permanganate in titrations. The oxidizing effect of the quadrivalent cerium cation depends on the reduction of the cerium to the trivalent condition. The ceric cation, Ce^{++++}, is reduced to Ce^{+++} about as easily as MnO_4^-

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[1] The valence of an ion containing more than one element is the algebraic sum of the polarities of its constituents. Except in peroxides, oxygen has a polarity of -2 in its compounds. The polarity of the chromium can be determined from the charge of the ion and that of the oxygen. The same is true of the permanganate ion or of any other complex ion. Thus, in $Cr_2O_7^{--}$ the chromium must have a polarity of $+6$ if each atom of oxygen has a polarity of -2, in order to get a charge of -2 on the $Cr_2O_7^{--}$.

is reduced to Mn^{++}. Ceric solutions are more stable than permanganate solutions, but the end point in a titration is not so easy to find. Usually it is best to determine the end point potentiometrically or with the aid of a colored substance that changes color when oxidized, such as diphenylamine or diphenylamine sulfonic acid.

$$Ce^{++++} + Fe^{++} = Ce^{+++} + Fe^{+++}$$
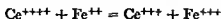
It is quite likely that the Ce^{++++} is present in a complex rather than as a simple ion.

The equivalent weight of a reducing agent is determined in like manner by the gain in polarity which the oxidized element experiences. Ferrous salts are oxidized to ferric salts, and the iron is changed from $+2$ to $+3$ in polarity. A normal solution of ferrous sulfate, $FeSO_4 \cdot 7H_2O$, or of ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, will contain 1 mole of either salt per liter.

As precipitants, the normal solutions are referred to the simplest type of salt in which each constituent has a valence of 1. Thus, of sodium chloride, $NaCl$, and of silver nitrate, $AgNO_3$, a normal solution will contain 1 mole per liter. Of sodium sulfate, Na_2SO_4, barium chloride, $BaCl_2$, and magnesium sulfate, $MgSO_4$, a normal solution will contain ½ mole per liter.

If potassium dichromate is used as a precipitant in the following reaction

$$Cr_2O_7^- + 2Ba^{++} + 2C_2H_3O_2^- + H_2O \rightarrow 2BaCrO_4 + 2HC_2H_3O_2$$
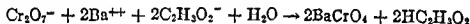
the normal solution will contain ¼ mole per liter.

Oxalic acid and the acid oxalates are used sometimes as acids and sometimes as reducing agents. Oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, has 2 replaceable hydrogens when titrated against alkali with phenolphthalein as indicator, and its normal solution as an acid contains ½ mole per liter:

$$H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O$$

or

$$2H^+ + 2OH^- \rightarrow 2H_2O$$
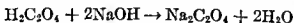
Oxalic acid also reacts with permanganate in accordance with the following equation:

$$5C_2O_4^- + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{++} + 8H_2O + 10CO_2$$
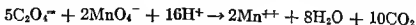
From the fact that the normal solution of permanganate contains ⅕ mole per liter, it is clear that the equivalent weight of oxalic acid as a reducing agent is ½ mole, just as when acting as an acid. In this case, however, the reducing power has nothing whatever to do with the hydrogen-ion content of oxalic acid, for the above reaction takes place

in the presence of a mineral acid. The valence of carbon in oxalic acid is 4, and the structural symbol, leaving out the water of crystallization, is written thus:

$$O = C - O - H$$
$$\mid$$
$$O = C - O - H$$
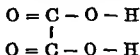
This structural symbol shows that 3 valence bonds of each carbon atom are positive toward 2 atoms of oxygen but one bond of each carbon atom is neutralized by a valence bond of the other carbon atom. The effective valence of each carbon atom is therefore $+3$ toward O or OH. It becomes $+4$ when oxidized to CO_2. When oxalic acid is heated alone, H_2O, CO, and CO_2 are formed, and thus, without oxidation, bivalent and quadrivalent carbon atoms appear which correspond to the above assumption of an average polarity of $+3$.

That the equivalent of $C_2O_4^{--}$ is ½ mole is also shown by the fact that the oxidation can be expressed by the equation

$$C_2O_4^{--} - 2\epsilon \approx 2CO_2$$
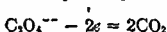
in which ϵ represents the unit charge of the electron.

Potassium acid oxalate, KHC_2O_4, can be used as an acid

$$KHC_2O_4 + KOH \rightarrow K_2C_2O_4 + H_2O$$
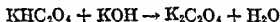
in which case the equivalent weight is 1 mole of KHC_2O_4, but as a reducing agent the reducing power is due to the oxalate anion and a normal solution will contain only ½ mole of KHC_2O_4. A solution of KHC_2O_4 which is normal as an acid will be $2 N$ as a reducing agent.

Potassium tetroxalate behaves similarly. As an acid it has 3 replaceable hydrogens and the equivalent weight is ⅓ mole:

$$KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O + 3NaOH \rightarrow KNaC_2O_4 + Na_2C_2O_4 + 5H_2O$$
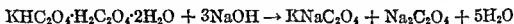
As a reducing agent, potassium tetroxalate has two $C_2O_4^{-}$ groups and the equivalent weight is ¼ mole. If a solution of potassium tetroxalate contains 1 mole per liter, it is $3 N$ as an acid and $4 N$ as a reducing agent, and the same relation holds at all concentrations.

Preparation of Normal Solutions

The required amount of substance should be dissolved in water and diluted to a volume of 1 l at 20°. Often, however, the water is

not at the normal temperature, so that it is customary to dissolve the substance in water at the laboratory temperature and then dilute the solution up to the mark in a liter flask. After the solution is thoroughly mixed its temperature is taken by a sensitive thermometer. If the temperature is above 20°, the volume of the solution would be less than 1 l if it were cooled to exactly 20°, so that the solution as made up is a little too strong. The following table shows how to correct for the temperature effect:

TEMPERATURE CORRECTION FOR VOLUMETRIC SOLUTIONS

Temp. of Measurement, °C	Capacity of Apparatus in Milliliters at 20°C						
	2000	1000	500	400	300	250	150
	Correction in Milliliters to Give Volume of Water at 20°C						
15	+1 54	+0 77	+0.38	+0.31	+0 23	+0.19	+0.12
16	+1 28	+0 64	+0 32	+0 26	+0.19	+0.16	+0 10
17	+0 99	+0 50	+0 25	+0 20	+0 15	+0.12	+0 07
18	+0 68	+0 34	+0 17	+0 14	+0.10	+0.08	+0.05
19	+0.35	+0 18	+0.09	+0 07	+0.05	+0.04	+0.03
21	−0.37	−0 18	−0.09	−0.07	−0.06	−0 05	−0 03
22	−0 77	−0 38	−0.19	−0.15	−0.12	−0.10	−0.06
23	−1 18	−0 59	−0.30	−0.24	−0 18	−0 15	−0 09
24	−1 61	−0 81	−0.40	−0 32	−0.24	−0 20	−0.12
25	−2 07	−1 03	−0.52	−0 41	−0 31	−0.26	−0.15
26	−2 54	−1 27	−0 64	−0 51	−0 38	−0 32	−0.19
27	−3 03	−1 52	−0.76	−0 51	−0 46	−0 38	−0 23
28	−3 55	−1 77	−0 89	−0 71	−0 53	−0.44	−0.27
29	−4 08	−2 04	−1 02	−0 82	−0 61	−0 51	−0 31
30	−4 62	−2 31	−1 16	−0 92	−0 69	−0 58	−0.35

[This table shows the correction to various observed volumes of water, measured at the designated temperatures, to give the volume at the standard temperature, 20°C. Conversely, by subtracting the corrections from the volume desired at 20°C, the volume that must be measured out at the designated temperature in order to give the desired volume at 20°C will be obtained. It is assumed that the volumes are measured in glass apparatus having a coefficient of cubical expansion of 0.000025 per degree centigrade. The table is applicable to dilute aqueous solutions having the same coefficient of expansion as water.]

For the following standard solutions more accurate results will be obtained if the numerical values of the above corrections are increased by the pereentages given below:

Solution	Normality		
	N	$0.5 N$	$0.1 N$
HNO₃.......	50	25	6
H₂SO₄......	45	25	5
NaOH.......	40	25	5
KOH.......	40	20	4
HCl........	25	15	3
H₂C₂O₄......	30	15	3
Na₂CO₃......	40	25	5

Standardization of Solutions

If the reagent to he used in a volumetric analysis is known to he pure, it is hest to prepare the standard solution as outlined on p. 446. Frequently, however, it is hetter to determine the concentration by testing the strength of the solution against some other suhstance known to he pure. Thus the strength of an aeid solution can he determined by weighing out some earefully purified sodium earhonate and determining exactly how much of the acid solution is required to neutralize this weight of pure sodium carhonate. In this ease the acid solution is said to he *standardized against* sodium carhonate and sodium carhonate is called the *standard* suhstance. Evidently, if the acid is a *normal* solution, each milliliter of solution will neutralize exactly 1 milliequivalent of the standard. The normal solution not only contains 1 milliequivalent of the active reagent in 1 ml hut also it will react witb 1 milliequivalent of other suhstances. In any standardization, therefore, if g is the weight of standard taken, ml is the number of milliliters of solution required to react with this weigbt of standard, and e is the milliequivalent weight of the standard used,[1] then the *normality* of the solution (or tbe number of milliequivalents in 1 ml) is $\dfrac{g}{ml \times e} = N$. Usually this is sufficient because the weight of suhstance that reacts with 1 ml of tbe standardized solution can he found by multiplying the milliequivalent weight of the suhstance analyzed by the value N. Sometimes, however, it is better

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[1] On p. 452, e was used to represent a unit of electricity, namely, a unit charge of 96,500 coulombs on a gram equivalent or 96,500 ÷ (6.06 × 10²³) coulombs or the actual atom or radical. Throughout the book, the italic letter e will be used in both ways, but this should not cause confusion.

to make the solution exactly normal, half-normal, or tenth-normal. To do this it is best to prepare the solution a little stronger than desired and then dilute it with water until the desired concentration is obtained. Then, if N is the normal concentration originally obtained, N' is the desired normality, V is the original volume taken, and V' is the volume after dilution, $N \times V = N' \times V'$ and $V' = (N \times V)/N'$. $V' - V$ is then the volume of water to be added to the volume V.

In volumetric work it is often desirable to have two solutions of reagents, one having the opposite effect to the other. Thus, in working with an acid, sometimes too much is added and it is convenient to have a standardized solution of a base at hand to neutralize the excess acid. It is not necessary to standardize the second solution independently, but it is important to know the relative strengths of the two solutions.

If a ml of solution A are equal in strength to b ml of solution B, then 1 ml of $A = b/a$ ml of B and 1 ml of $B = a/b$ ml of A. If solution A is N-normal, then solution B is $(a \times N)/b$ normal. If, on the other hand, the solution A is known to be N-normal and solution B is known to be M-normal, then the relative strengths are: 1 ml of solution $A = N/M$ ml of solution B; 1 ml of solution $B = M/N$ ml of solution A.

General Method of Computing Results

Let ml represent the volume in milliliters of N-normal solution required to react with s grams of a substance of which the milliequivalent weight is e; then

$$\frac{ml \times N \times e \times 100}{s} = \text{per cent}$$

In the analysis of sodium carbonate, molecular weight 106.0, completely neutralized by hydrochloric acid, the value of e is 0.0530 and the result obtained by the above formula will be the percentage of Na_2CO_3 in the sample analyzed. If it is desired to express the result in terms of Na_2O, molecular weight 62.0, the value of e is 0.0310. Or it may be desired to find the percentage of CO_2 in the sample on the assumption that nothing else but Na_2CO_3 is present that will react with the acid used. In this case the value of e is 0.022. In using the above formula, therefore, it is necessary to bear in mind that the value of the milliequivalent should be in terms of the substance desired. The value $N \times e$ is called the *titer* of the solution with respect to the substance of which e is the milliequivalent weight. Thus e for Na_2O is 0.0310 g, and for 0.5 N HCl the titer in terms of Na_2O is $0.5 \times 0.031 = 0.0155$ g Na_2O, which *means*

Sometimes, it is desirable to avoid computations in technical work and it is convenient to weigh out a sample such that the buret reading will give the percentage desired (cf. p. 17). This will always be true if the weight of sample is $100 \times N \times e$, as inspection of the above equation will show. Or, if the weight of sample is $50 \times N \times e$, then the desired percentage will be found by multiplying the ml used by 2.

CHAPTER XIV

ACIDIMETRY AND ALKALIMETRY

The useful reactions of analytical chemistry are those which take place practically completely in a given direction. Such reactions are those in which a slightly ionized substance is formed, an insoluble precipitate is obtained, a gas is evolved, or there is an oxidation of one substance at the expense of another. The law of chemical mass action applied to a reaction of the type $A + B \rightarrow C + D$ tells us that a reaction may be expected to go to completion if one of the products, either C or D, is removed as fast as it is formed, and this happens when the substance is not ionized, is insoluble, or is a gas. The reason that the reaction $NaOH + HCl = NaCl + H_2O$ takes place in dilute solutions is that water is ionized but slightly and, from the standpoint of the electrolytic dissociation theory, the reaction of neutralization is really

$$H^+ + OH^- = H_2O$$

This is shown by the fact that the heat evolved by the reaction in dilute solution is practically the same irrespective of the nature of the ions that were originally combined with the H^+ and OH^- provided that the original acid and base are both ionized almost completely.[1]

The mass-action law, applied to the ionization of water, tells us that a state of equilibrium exists when

$$\frac{[H^+] \times [OH^-]}{[H_2O]} = \text{a constant}$$

In these mass-action expressions, a symbol written inside a bracket signifies a concentration expressed in moles per liter. In the case of water, the concentration of the non-ionized H_2O is not changed appreciably as a result of ionization at room temperatures, and its concentration is enormous compared to the concentration of its ions; the above expression can be simplified, therefore, by saying $[H^+] \times [OH^-] = K_w = 1.0 \times 10^{-14}$ at 21°. This expression is of fundamental importance. It states that in any aqueous solution the concentration of hydrogen ions

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[1] Most ions are hydrated. For this reason, some textbooks insist on the use of the *hydronium* ion, H_3O^+, in place of the hydrogen ion, H^+. H_3O^+ also has been called the *oxonium* ion.

(expressed in moles per liter) multiplied by the concentration of the hydroxyl ions present (also expressed in moles per liter) always equals 1.0×10^{-14} at $24°$.[1] Since 1 mole of H^+ and 1 mole of OH^- are formed from each mole of ionized water, it is evident that, in absolutely neutral water, the concentration of each of these ions is 1.0×10^{-7} at $24°$.

Very small numbers such as these are handled conveniently with logarithms. Since the cologarithm, or *negative logarithm* as it is often called, is the logarithm of the reciprocal of a number, it can be used equally well. Usually we multiply two numbers by adding their logarithms, but we get the same answer if we subtract the negative logarithm of one from the logarithm of the other. Similarly, the value a/b can be found by adding the negative logarithm of b to the logarithm of a. If c is the concentration of H^+ ions, $\log 1/c$ or $-\log c$ is called the *pH* or *hydrogen exponent* of the solution. Pure water at $24°$ has $pH = 7$, $pOH \approx 7$, and $pK_w = 14$. This pH concept is widely used. In general, if the pH exceeds 7 the solution is more basic than water, and when $pH < 7$ it is more acidic than water.

Since in any solution at $24°$ $[H^+] \times [OH^-] = 1.0 \times 10^{-14}$, it is clear that the concentration of the OH^- is known as soon as the concentration of the H^+ is stated. In all cases $pH + pOH = 14$ at $24°$.

Logarithms. Almost every reader of this book will have used logarithms in connection with the study of algebra or trigonometry, but there may be some who have forgotten how to use logarithms with respect to expressions like $1/[H^+]$.

A logarithm of a number expresses the number as a power of some other number known as the base. Logarithms to the base 10, called *common logarithms* (Briggs), are used to simplify calculations; the expression $\log a$ always means the logarithm of the number a to the base 10 unless otherwise stated. If the number in question is an exact power of 10, it is easy to find the logarithm, as the following table shows:

Number...	1,000	100	10	1	0.1	0.01	0.001
Exponential form	10^3	10^2	10^1	10^0	10^{-1}	10^{-2}	10^{-3}
Logarithm	3	2	1	0	-1	-2	-3

A logarithm is said to have two parts, the *characteristic* and the *mantissa*. The characteristic is a whole number which is written to the left of the decimal point in the logarithm, and the mantissa is the decimal fraction which is written to the right of the decimal point. The characteristic is used to locate the decimal point, and the mantissa gives the significant digits of the number. A simple example will explain this, using the number 25 with various positions of the decimal point.

Number.... .	2500	250	25	2.5	0.25	0.025	0.0025
or..........	2.5×10^3	2.5×10^2	2.5×10	2.5	2.5×10^{-1}	2.5×10^{-2}	2.5×10^{-3}
Logarithm....	3.3979	2.3979	1.3979	0.3979	$\bar{1}.3979$	$\bar{2}.3979$	$\bar{3}.3979$

[1] The ionization constant of water, K_w, varies from 0.12×10^{-14} at $0°$ to 73×10^{-14} at $100°C$. pK_w varies from 14.92 to 12.14.

tbe denominator, it is evident tbat the cologarithm of a number is found by subtracting its logarithm from zero. Thus the log of 2 = 0.3010, and its cologarithm is $\overline{1}.6990$ (tbe log of 0 5 which is the reciprocal of 2). The mantissas of tbese cologarithms (usually called *cologs*) can be written directly from the values in the table by subtracting each digit from 9 except the last on the right (other tban 0) which is subtracted from 10. In a series of multiplications and divisions it is often advantageous to use the cologarithms because adding the cologarithm has the same effect as subtracting the logarithm and the series can be carried out by a single addition of all the values. Cologarithms are sometimes called *negative* logarithms because they are obtained by subtracting the logarithms from 0.

Finding pH Values. From what has just been said, it is evident that pH values represent the cologarithms of hydrogen-ion concentrations expressed in moles per liter. If the hydrogen-ion concentration is an even power of 10, the pH value is at once apparent. Thus $pH = 7$ means that the hydrogen-ion concentration is 10^{-7} mole per liter. What will be the pH of a solution containing, let us say, 0.000023 mole of H^+ per liter? The logarithm of 0.000023 is 5.36, and the cologarithm is 4 64.[1] To find pH values corresponding to solutions containing less tban 1 mole H^+ per liter, express the moles per liter as a whole number between 0 and 10 multiplied by 10 to a negative power. Then, if this number is $a \times 10^{-b}$, look up the logarithm of a in the table to two significant figures (or take it from a slide rule), and subtract this value from b.

Conversely to find the concentration in moles of H^+ per liter to correspond to $pH = 4.64$, subtract 4.64 from 0.00 and get 5.36, look up the number corresponding to 0.36 ($= 2.3$), and write $2 3 \times 10^{-5}$ as the desired number.

A perfectly neutral solution has a pH value of 7. If the pH value is smaller than 7, the solution can he said to be more acidic than pure water, and if it is larger than 7 it is more basic. Another way of expressing this is to say that a solution is acidic if it contains more hydrogen ions per unit volume than are present in pure water and basic if it contains fewer hydrogen ions. It is well known that acids and bases vary greatly with respect to their ionization in aqueous solutions. The relative strength is shown by a comparison of the ionization constants.[2]

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[1] This is easily seen by expressing 0.000023 as 2.3×10^{-5}. Then

$$\frac{1}{2.3 \times 10^{-5}} = \frac{10^5}{2.3} \quad \text{and} \quad \log \frac{10^5}{2.3} = \log 10^5 - \log 2.3 = 5\ 00 - 0\ 36 = 4.64.$$

[2] The mass-action law applied to the ionization of a weak acid takes the general form $\frac{[H^+] \times [A^-]}{[HA]} = k$, in which k is called the *ionization constant*. Dibasic and tribasic acids are usually ionized to different degrees witb respect to each replaceable hydrogen atom. The primary ionization constant of H_3PO_4 is $\frac{[H^+] \times [H_2PO_4^-]}{[H_3PO_4]} = 1.1 \times 10^{-2}$; the secondary ionization constant is $\frac{[H^+] + [HPO_4^{--}]}{[H_2PO_4^-]} = 2.0 \times 10^{-7}$; and the tertiary ionization constant is $\frac{[H^+][PO_4^{---}]}{[HPO_4^{--}]} = 3 6 \times 10^{-12}$.

The value 3.6×10^{-12} for the tertiary ionization of phosphoric acid shows that the presence of a considerable quantity of HPO_4^- in an aqueous solution does not increase

When a strong acid, like hydrochloric acid, is neutralized with a strong base, such as sodium hydroxide, the reaction takes place practically completely as soon as exactly one equivalent of the base has been added. There is no appreciable hydrolysis of the salt formed, and the end point takes place at pH = 7. It is a different matter when a weak acid like acetic acid is neutralized with sodium hydroxide. In this case the sodium acetate as it is formed tends to repress the ionization of the unneutralized acid, and when, finally, a quantity of base equivalent to the original acetic acid has been added, the pH of the solution will be distinctly higher than 7. In the same way, when sodium acetate is dissolved in water, the solution will show pH > 7. If a weak base like NH$_4$OH is neutralized with a strong acid like hydrochloric acid, the final solution will show a pH distinctly less than 7.

Titration of 0.1 N HCl with 0.1 N NaOH   Titration of 0.1 N HC$_2$H$_3$O$_2$ with 0.1 N NaOH   Titration of 0.1 N HC$_2$H$_3$O$_2$. with 0.1 N NH$_4$OH.
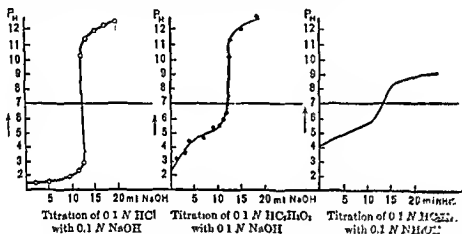
FIG. 80.

The curves of Fig. 80, obtained by measurement of the single(?) of a hydrogen electrode during a titration, illustrate the?? curve for the titration of the hydrochloric acid with sodium shows a marked change produced by a very little ba?? point is reached. This may be taken as the halfway p?? vertical line and corresponds almost exactly to pH = 7?? the titration of the acetic acid shows a distinct rise in ?? end point is reached, and the halfway point of the ??

very much the concentration of the hydrogen ions present o?? as a result of the ionization of water itself.

The mass-action law applied to the ionization of a ?? does not give a useful value because, if the *ionizatio*?? value of the ionization constant ?? es ∞. In ?? stants, therefore, it is customary ?? t of the ?? number is enclosed in brackets ?? t is ?? of the mass-action law.

at a $pH > 7$. The third curve shows an indistinct end point, although the solution is neutral with $pH = 7$ when an equivalent of hase has been added. The indistinct end point is due to the fact that the ionization of hoth acid and the base is slight in the presence of their neutral salt; as a result, ammonium acetate is hydrolyzed appreciably in aqueous solution.

From what has just been said four conclusions can he drawn: (1) the end point of a titration of an acid with a base does not always coincide with $pH = 7$; (2) a good end point cannot be obtained if both the acid and the hase are weak; (3) when a weak acid is titrated with a strong base, the end point occurs at $pH > 7$; and (4) wben a weak hase is titrated with a strong acid the end point occurs at $pH < 7$.

INDICATORS

The indicators used in acidimetry and alkalimetry are dyestuffs which are of one color in acid solutions and another color in basic solutions. They are, as a rule, weak acids, though some of them are weak bases. It has heen found that in organic compounds the color can usually he traced to a particular arrangement of atoms called a *chromophor*. The change in color, therefore, is caused by a slight rearrangement of the atoms in the molecule. Thus, if the salt of an indicator acid is yellow and on treatment with acid it turns red, the change in color is due to the fact that, when the indicator acid is liberated hy the action of the stronger acid, the molecule undergoes a slight change in tbe way the atoms are linked together and thereby loses temporarily the ability to ionize as an acid. It is not sufficient, however, to assume that this change of color is caused solely by the fact that the ions have a color other than that of the undissociated molecule; on the contrary, it has heen shown in certain cases that the ions have the same color that tbe undissociated molecule has before the rearrangement of the atoms in the molecule has taken place. On tbe other hand, as regards tbe proper use of indicators it is necessary simply to bear in mind how salts of weak acids behave in the presence of stronger acids and how tbe acids themselves behave in tbe presence of alkali.

By means of electrometric tests it is possible to determine tbe hydrogenion concentration at which any indicator changes color. Indicators are known which cbange at different concentrations of bydrogen ion, and for any special case an indicator should be chosen whicb will cbange color as nearly as possible at the bydrogen-ion concentration corresponding to the saturation point of the acid and base used in tbe analysis.

Indicators may be classed as *neutral* when tbey cbange color at about pH 7, *sensitive to acids* when the transition interval is distinctly greater than pH 7, and *sensitive to bases* if tbey change color at values distinctly

below pH 7. With absolutely pure water, containing no dissolved CO_2, the first class show the transition tint, the second class show their acid colors, and the third show their basic tints. In other words, water is neutral to the first, acid to the second, and basic to the third class. Water saturated with CO_2 under a pressure of 1 atmosphere of this gas has a pH of about 3.7 at 25°; water in contact with a normal atmosphere containing about 0.03 per cent by volume of CO_2 has a pH of about 5.7; and carefully prepared conductivity water has a pH close to 7.

Innumerable organic compounds containing acid or basic groups change color at definite concentrations of H^+, and it is possible to select indicators so that a fairly close estimation of the pH can be made from pH 1 to pH 14. The following table shows the color-change intervals of some of the most-used indicators. Some indicators, like thymol blue, have two transitions because of the presence of more than one group sensitive to acid or base.

COLOR-CHANGE INTERVALS OF CERTAIN ACID-BASE
INDICATORS AT 25°

Chemical Name	Trade Name	Color Change Acid-Base	pH Range
Thymol-sulfonphthalein	Thymol blue	Red-yellow	1 2- 2.8
Diphenylamino-p-benzene sodium sulfonate	Tropeolin 00	Red-yellow	1.3- 3.0
Dimethylaminoazobenzene	Methyl yellow	Red-yellow	2.9- 4.0
Tetrabromophenol-sulfon-phthalein	Bromophenol blue	Yellow-purple	3.0- 4.6
Dimethylaminoazobenzene sodium sulfonate	Methyl orange	Red-orange-yellow	3.1- 4.4
Tetrabromophenol-m-cre-sol-sulfonphthalein	Bromocresol green	Yellow-blue	3 9- 5.4
p-Dimethylaminoazoben-zene-o-carboxylic acid	Methyl red	Red-yellow	4.2- 6 2
Dichlorsulfonphthalein	Chlorophenol red	Yellow-red	4.8- 6.4
Dibromothymol-sulfon-phthalein	Bromothymol blue	Yellow-blue	6 0- 7.0
Phenol-sulfonphthalein	Phenol red	Yellow-red	6 4- 8.0
Dimethyldiaminophenazine chloride	Neutral red	Red-yellow-orange	6 8- 8.0
m-Cresol-sulfonphthalein	m-Cresol purple	Yellow-purple	7.4- 9.0
Thymol-sulfonphthalein	Thymol blue	Yellow-blue	8 0- 9.6
Phenolphthalein	Phenolphthalein	Colorless-red	8.0- 9.8
Thymolphthalein	Thymolphthalein	Colorless-blue	9.3-10.5
Na salt of p-nitraniline-azosalicylic acid	Alizarin yellow	Yellow-violet	10 1-12.0

Suitable indicator solutions contain 0 05-0.1 g of the solid in 100 ml

dissolved in water. Methyl yellow, neutral red, phenolphthalein, and thymolphthalein are soluble in 90 per cent alcohol. The sulfonphthaleins dissolve in water after an equivalent quantity of sodium hydroxide has been added to form the water-soluble sodium salt. Triturate 0.1 g of the powder with the following volumes of 0.1 N NaOH: thymol blue, 2.15 ml; bromophenol blue, 1.5 ml; bromocresol green, 1.45 ml; methyl red, 3.7 ml; chlorophenol red 2.35 ml; bromothymol blue, 1.6 ml; phenol red, 2.85 ml; cresol purple, 2.6 ml. Dissolve in water and dilute to 100 ml.

It was stated on p. 462 that some indicators changed color at pH values distinctly below 7 and were sensitive to weak bases, others changed at about pH 7, and others changed at pH distinctly greater than 7. This, however, does not mean that the indicators themselves are acid, neutral, or basic in such a grouping. Some indicators contain both acid and basic groups in their molecules. Methyl orange, which changes color at pH 3.1–4.4, is an acid which is stronger than acetic acid; phenolphthalein is an acid comparable in strength to boric acid; methyl orange is sensitive to bases, and phenolphthalein to acids. Methyl yellow is a weak base with ionization constant 1×10^{-11}. As a general rule, the fact that an indicator is sensitive to bases and changes color at a pH below 7 indicates that the indicator itself is either a relatively strong acid or a weak base. Some writers call methyl orange a weak base and others classify it as an acid. The dimethylaminoazobenzene sulfonic acid itself is distinctly acidic for the SO_3H group is much stronger as an acid than the substituted amino group as a base, but the sodium salt of dimethylaminoazobenzene sulfonic acid behaves like a weak base. It is a base in the sense that any salt of a weak acid, like sodium acetate for example, is a weak base, and, as a matter of fact, the Brönsted definition of acid and base does make the acetate ion a base. It is idle, therefore, to argue whether the different indicators are themselves acids or bases. Many of them are weak acids which are present as sodium salts in the indicator solutions.

It is sometimes desirable to have at hand solutions of definite pH values. These so-called *buffer solutions* can be prepared from carefully standardized 0.2 N HCl, 0.1 N HCl, 0.1 N NaOH, and 0.1 M solutions of potassium acid phthalate, monopotassium phosphate, potassium chloride, and boric acid. To prepare 100 ml of the last four solutions, dissolve separately 2.042 g KHC₈H₄O₄, 1.362 g KH₂PO₄, 0.746 g KCl, and 0.62 g H₃BO₃ in water, dilute each solution to exactly 100 ml in a volumetric flask, mix, and store in glass-stoppered bottles. To prepare solutions of definite pH mix these solutions in accordance with the following table.[1]

[1] W. M. Clark, *The Determination of Hydrogen Ions*, 3rd ed., 1928.

Composition	*p*H
48 5 ml 0.2 *N* HCl + 25 ml 0.2 *N* KCl diluted to 100 ml....	1.0
32.25 " " " " " " " " "	1.2
20.75 " " " " " " " " "	1.4
13.15 " " " " " " " " "	1.6
8.3 " " " " " " " " "	1.8
5 3 " " " " " " " " "	2.0
3.35 " " " " " " " " "	2 2
46 70 ml 0.1 *N* HCl + 50 ml 0.1 *M* KHC₂H₄O₄ diluted to 100 ml....	2.2
39 60 " " " " " " " " "	2.4
32.95 " " " " " " " " "	2 6
26.42 " " " " " " " " "	2 8
20.32 " " " " " " " " "	3 0
14.70 " " " " " " " " "	3 2
9 90 " " " " " " " " "	3.4
5 97 " " " " " " " " "	3 6
2.63 " " " " " " " " "	3 8
0 40 ml 0 1 *N* NaOH + 50 ml 0 1 *M* KHC₂H₄O₄ diluted to 100 ml....	4.0
3 70 " " " " " " " " "	4 2
7.50 " " " " " " " " "	4 4
12 15 " " " " " " " 7₄ "	4 6
17 70 " " " " " " " " "	4 8
23 85 " " " " " " " " "	5.0
29 95 " " " " " " " " "	5.2
35 45 " " " " " " " " "	5.4
39 85 " " " " " " " " "	5.6
43.00 " " " " " " " " "	5.8
45 45 " " " " " " " " "	6.0
5 70 ml 0 1 *N* NaOH + 50 ml 0 1 *M* KH₂PO₄ diluted to 100 ml....	6.0
8 60 " " " " " " " " "	6.2
12 60 " " " " " " " " "	6.4
17 80 " " " " " " " " "	6 6
23 65 " " " " " " " " "	6 8
29.63 ml 0.1 *N* NaOH + 50 ml 0 1 *M* KH₂PO₄ diluted to 100 ml....	7.0
35 00 " " " " " " " " "	7.2
39 50 " " " " " " " " "	7.4
42 80 " " " " " " " " "	7.6
45 20 " " " " " " " " "	7.8
46 80 " " " " " " " " "	8.0
2 61 ml 0 1 *N* NaOH + 50 ml 0 1 *M* H₃BO₃ diluted to 100 ml.... ..	7 8
3 97 " " " " " " " " "	8 0
5 90 " " " " " " " " "	8.2
8 50 " " " " " " " " "	8 4
12 00 " " " " " " " " "	8 6
16 30 " " " " " " " " "	8 8
21.30 " " " " " " " " "	9 0
26.70 " " " " " " " " "	9 2
32.00 " " " " " " " " "	9 4
36 85 " " " " " " " " "	9 6
40 80 " " " " " " " " "	9.8
43.90 " " " " " " " " "	10.0

Mixed Indicators. An indicator which has one color in an acid solution and another color in a basic solution does not show a pronounced sharp color change at a definite pH but there is a gradual changing of the color over a transformation range. Thus methyl orange is changing color from pH 3.1 to 4.4. A sharper transformation, and one that is easier for most eyes to detect, can be obtained if some dyestuff is added of a color complementary to one of the indicator colors. Such mixed indicators have been often proposed[1] though not much used. Especially useful is a mixture of 1 g of methyl orange and 1.4 g of xylene cyanole FF in 1 l of 50 per cent ethyl alcohol. The color is green in a basic solution and magenta in an acid solution. The mixture is neutral gray at pH 3.8.

For a rapid and approximate determination of the pH a so-called *universal indicator* can he used. Universal indicators are mixtures of dyestuffs so chosen that the mixture assumes a different color at each different unit of pH. Thus Kolthoff has recommended a mixture of 15 ml 0.1 per cent dimethylaminoazobenzene + 5 ml of 0.1 per cent methyl red + 20 ml 0.1 per cent bromothymol blue + 20 ml of 0.1 per cent phenolphthalein + 20 ml of 0.1 per cent thymolphthalein. The colors obtained when 0.1 ml of the mixture is added to 10 ml of the solution to be tested are: rose at pH 2.0; reddish orange at pH 3.0; orange at pH 4.0; yellow-orange at pH 5.0; lemon-yellow at pH 6.0; yellow-green at pH 7.0; green at pH 8.0; blue-green at pH 9.0; and violet at pH 10. Such mixtures can be purchased but are not very accurate.

The indicators most used in quantitative analysis are *methyl orange, methyl red,* and *phenolphthalein.*

1. Methyl Orange

By methyl orange,[2] Lunge,[3] who first proposed the use of this indicator, understood either the free sulfonic acid of dimethylaminoazobenzene or its sodium or ammonium salt.

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[1] M. Scholtz, *Z. Elektrochem.,* **10,** 549 (1904); Luther, *Chem.-Ztg.,* **31,** 1172 (1907); Kirschnik, *Chem.-Ztg.,* **31,** 960 (1907); A. Cohen, *J. Am. Chem. Soc.,* **44,** 185 (1922); Hickman and Linstead, *J. Am. Chem. Soc.,* **121,** 2502 (1922); Lizius, *Analyst,* **46,** 355 (1921); F. H. Carr, *Analyst,* **47,** 196 (1922); G. Simpson, *J. Ind. Eng. Chem.,* **16,** 709 (1924); I. M. Kolthoff, *Säure-Base Indicatoren;* Kolthoff-Rosenblum, *Acid Base Indicators.*

[2] This dyestuff has been known commercially as helianthin, orange III, tropeolin D, Poirrier's orange III, dimethylaniline orange, mandarin orange, and gold orange.

[3] *Ber.,* 1878, II, 1944; *Chem. Ind.,* **1881,** 348; *Handbuch für Sodaindustrie,* I, 52 (1879); II, 151 (1893).

In the free state, the sulfonic acid is obtained in the form of reddish violet scales, soluble in considerable water. If some of the solid is dissolved in as little water as possible, a distinct reddish orange solution is obtained; but on the further addition of water this color gradually changes to yellow. If a trace of an acid is added to the yellow solution, it becomes red again, and on further dilution with water the color changes to orange and finally to yellow once more, if too much acid was not added. The color changes which take place between $pH = 3.1$–4.4 can be explained easily.

In the sensitive neutral solution there is a condition of equilibrium between two isomeric forms of methyl orange as expressed by the equation:

$$HSO_3 \cdot C_6H_4 \cdot N:N \cdot C_6H_4N(CH_3)_2 \rightleftarrows SO_3 \cdot C_6H_4 \cdot NH \cdot N:C_6H_4 \cdot N(CH_3)_2$$
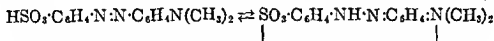
The formula on the left represents the yellow substance and the color is due to the azo group $N:N$, whereas the formula on the right represents the red substance which has for its chromophor the quinoid group $:C_6H_4:$. The formula on the left has a sulfonic group which imparts acid properties to the molecule, and at the other end is an $N(CH_3)$ group which has weakly basic properties. The formula on the right, therefore, represents an inner salt inasmuch as the acid- and base-forming groups are united.

The sodium salt of methyl orange is yellow and has the formula

$$NaSO_3 \cdot C_6H_4N:NC_6H_4N(CH_3)_2$$

and when decomposed by acids the free sulfonate at once reverts to the red form:[1]

$$SO_3 \cdot C_6H_4 \cdot NH \cdot N:C_6H_4 \cdot N(CH_3)_2$$
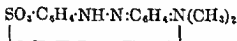
Methyl orange is an excellent indicator for weak bases but cannot be used for the titration of weak acids.

If it is desired to titrate a solution containing sodium hydroxide with a tenth-normal acid, add a little methyl orange to the alkaline solution and titrate with acid until the solution is colored a distinct red. This color will not appear permanently until an excess of the acid has been added. The use of excess acid causes a slight error in the analysis which is greater in proportion to the amount of indicator employed, and to the dilution of the solution.

From what has been said the following rule holds:

[1] Cf. Stieglitz, *J. Am. Chem. Soc.*, **25**, 1117; Peters and Redmon, *J. Chem. Education*, **17**, 525 (1910)

In any titration a small amount of indicator should be used, and, inasmuch as the change of color is proportional to the concentration and not to the absolute amount of acid present, the analyzed solution should have as nearly as possible the same concentration as prevailed in the standardization of the reagent used.

If a normal acid is used for the titration, the change of color is very sharp when the volume of the solution titrated amounts to about 100 ml. Even with a fifth-normal solution the change of color is very distinct, but less so with tenth-normal solutions; but these can be titrated provided the standardization was made at the same dilution as that used in the analysis.

How is it with the end point in the titration of an acid with an alkali hydroxide solution?

If a few drops of methyl orange are added to 100 ml of water, the water will be colored distinctly yellow. If the solution contains the same amount of hydrochloric acid as is contained in 10 ml of a tenth-normal solution of this acid, the solution will be colored a deep red. In order that the solution shall assume its original yellow color, it is only necessary to add exactly 10 ml of 0.1 N alkali hydroxide solution, but no excess of alkali, because the water is itself sufficient to decompose the dyestuff sufficiently to produce the yellow color.

It is evident, then, that it is not a matter of indifference in the analysis whether the titration is completed by the addition of acid or by the addition of alkali. In the former case, for the titration of T ml of 0.1 N alkali solution, $T + t$ ml of 0.1 N acid would be necessary.

Methyl orange is more sensitive toward alkali than toward acid, but many prefer to finish the titration by the addition of acid, for most eyes can detect the change from yellow to red with greater accuracy. In principle it is more accurate to accomplish the titration the other way, as was recommended by F. Glaser.

Uses. Methyl orange is suitable for the titration of strong acids (HCl, HNO_3, H_2SO_4) as well as phosphoric and sulfurous acids. Hydrochloric and nitric acids can be titrated with this indicator with a sharper end point than sulfuric acid.

Phosphoric Acid. If free phosphoric acid is titrated with sodium hydroxide in the presence of this indicator, the solution changes from red to yellow when one-third of the phosphoric acid has been neutralized:

$$H_3PO_4 + OH^- \rightleftharpoons H_2PO_4^- + H_2O$$

The primary phosphates are neutral toward methyl orange; the secondary and tertiary phosphates react alkaline toward it. With half-normal solutions, the end point of the reaction is fairly sharp. With

tenth-normal solutions it is less so, and an excess of about 0.3 ml of the 0.1 N alkali hydroxide is necessary to cause the change from red to yellow.

Sulfurous Acid. In titrating sulfurous acid with sodium hydroxide, the yellow color is obtained when half the acid has been neutralized

$$H_2SO_3 + OH^- = HSO_3^- + H_2O$$
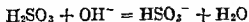
and HSO_3^- is neutral toward this indicator.

The weak acids HCN, H_2CO_3, H_2S, H_3AsO_3, H_3BO_3, and $HCrO_4^-$ when present in moderate quantities do not affect the color of methyl orange solutions. CO_2 and H_2S produce an orange-red coloration only when present in large amounts. For this reason dilute solutions of the alkali salts of these acids can be titrated with accuracy by means of this indicator.

Organic acids cannot be titrated with methyl orange.

The strong and weak bases NaOH, KOH, NH_4OH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$, and $Mg(OH)_2$ can be titrated with great accuracy by means of this indicator, and the same is true of the amine bases (methyl and ethyl amines, etc.); on the other hand, such weak bases as pyridine, aniline, and toluidine cannot be titrated.

Nitrous acid ordinarily cannot be titrated with this indicator because the acid destroys it. If, however, an excess of alkali is first added to the solution of nitrous acid, then the methyl orange, the titration can be accomplished with accuracy.

2. Methyl Red

$$(CH_3)_2\overset{4}{N} - C_6H_4 - \overset{3}{N} = \overset{2}{N} - C_6H_4 - \overset{1}{COOH}$$
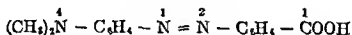
Paradimethylaminoazobenzene-o-carboxylic acid

This valuable indicator is suitable for titrating weak organic bases and ammonia. The aqueous solution of methyl red is orange, but, if a few drops are added to 50–100 ml of water, the water is colored a pale yellow. The addition of a drop of 0.1 N HCl at once turns the liquid a violet-red without its passing through any intermediate shade, and by the addition of a drop of ammonia the solution becomes nearly colorless again. Methyl red is not very sensitive toward carbonic acid, but more so than methyl orange, so that it is less suitable for the titration of carbonates. The chief advantage of this indicator lies in the sharp color change from a very pale yellow to a violet-red, even in titrating ammonia. The color change is at pH = 4.2–6.2.

3. Phenolphthalein

Phenolphthalein is a very weak acid forming red salts which contain the strongly chromophoric quinoid group: C_6H_4:. The free acid, however, is unstable and, when set free from one of its colored salts, by the addition of acid, it reverts instantly into a colorless lactoid form, containing no chromophor group:

$$HOOC \cdot C_6H_4 \cdot C(C_6H_4OH):C_6H_4:O \rightleftharpoons O \cdot OC \cdot C_6H_4 \cdot C(C_6H_4OH)_2$$

red   colorless
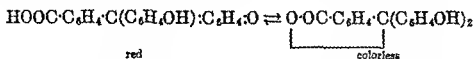
In the free acid, therefore, the condition of equilibrium favors the lactoid form and only traces of the quinoid acid are present. This trace of quinoid acid is ionized somewhat and is in equilibrium with its ions:

$$HOOC \cdot C_6H_4 \cdot C(C_6H_4OH):C_6H_4:O$$
$$\rightleftharpoons H^+ + OOC \cdot C_6H_4 \cdot C(C_6H_4OH):C_6H_4:O^-$$
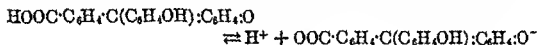
The addition of an alkali causes the hydrogen ions to disappear, so that more of the quinoid molecules must be ionized to preserve equilibrium, and the quinoid molecules in turn are reproduced from the lactoid as fast as the former are converted into the salt. Phenolphthalein is a very sensitive indicator towards acids, but on account of being a very weak acid it does not form stable salts with weak bases.

Phenolphthalein becomes pink in solutions of pH greater than 8.3 but becomes colorless in solutions which contain a large excess of alkali hydroxide. Potentiometric titrations indicate that phenolphthalein is tribasic and that the colorless forms are shown by free phenolphthalein and by the ion of tribasic salt. These facts and the theory that the color is due to *resonance*, or vibration in the molecule, can be explained as follows [1] Phenolphthalein in the unneutralized state has a colorless molecule that can be represented by the formula shown below in (*a*). The addition of OH^- causes the formation of H_2O with one of the phenol groups, but this causes disruption of the lactone group and the negative charge on the anion formed shifts to the carboxyl group giving the compound shown at (*b*). But the second phenol group is about as strongly acidic as the other, and it reacts with a second molecule of OH^- before the first reaction is completed, and this results in the formation of the dibasic anion shown in (*c*) The part of the compound containing the two phenol groups is now symmetrical, and the two resonance forms are shown in (*c*) and (*d*). The addition of strong caustic alkali forms the tribasic salt of phenolphthalein, and the colorless tribasic anion shown in (*e*) results in which no resonan e is possible.

[1] Peters and Redmon, *J Chem. Education*, **17**, 525 (1940).

(a) (b) (c) (d) (e)
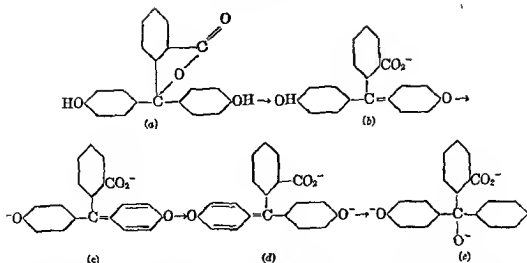
Uses. Phenolphthalein is particularly suited for the titration of organic and inorganic acids and strong bases, but not for the titration of ammonia.

If the red-colored solution containing phenolphthalein and a little alkali is treated with an excess of concentrated alkali hydroxide solution, the red color disappears at $pH = 10$ but returns if the solution is diluted with water. Phenolphthalein, therefore, cannot be used as an indicator for the titration of concentrated alkali without previous dilution with water.

Phenolphthalein is a sensitive indicator toward acids. It is far more sensitive to acids than is methyl orange, for not only can the presence of weak acids be detected, but even very small amounts can be titrated with accuracy.

Ordinary distilled water usually contains carbon dioxide, as can be shown by slowly adding 0.1 N barium hydroxide solution, drop by drop, to 100 ml of water containing a drop of the indicator solution. Where the alkali first meets the water, a red color is produced which disappears on stirring, so that often as much as 0.5 to 1.8 ml of the alkali must be added before a permanent red color is obtained. The disappearance of the red shows the presence of acid (in this case carbonic acid), and its amount corresponds to the alkali neutralized.

Phosphoric Acid. If a solution of phosphoric acid containing phenolphthalein is titrated with normal sodium hydroxide solution, a permanent coloration is produced when two-thirds of the phosphoric acid is neutralized:

$$H_3PO_4 + 2OH^- \rightarrow HPO_4^{--} + 2H_2O$$
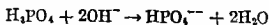
Apparently Na_2HPO_4 reacts neutral toward phenolphthalein, but this is not quite correct, for a pure solution of disodium phosphate is colored

a pale pink by phenolphthalein, and on dilution with water the intensity of the color increases owing to progressive hydrolysis:

$$HPO_4^{--} + H_2O \rightleftarrows OH^- + H_2PO_4^-$$
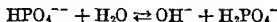
During the titration of phosphoric acid with sodium hydroxide, a pale pink color is obtained somewhat too soon, and this color gradually increases in intensity until finally a maximum is reached, which is taken as the end point. It is possible that this hydrolysis could be prevented by the addition of a large excess of sodium chloride and cooling to about 0°C.

Carbonic Acid. If the solution of a neutral alkali carbonate is treated with phenolphthalein a red color is obtained, showing the presence of hydroxyl ions in the solution, due to hydrolysis:

$$CO_3^{--} + H_2O \rightleftarrows OH^- + HCO_3^-$$
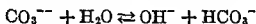
If hydrochloric acid is added to such a solution which is not too dilute and is at a temperature of 0°, decolorization is effected when the alkali carbonate[1] is changed to bicarbonate. At ordinary temperatures a sharp end point cannot be obtained; the color gradually fades. Pure sodium bicarbonate dissolved in ice-cold water is not colored by the addition of phenolphthalein; if it is warmed to the temperature of the room it turns red, but on cooling the color disappears (Küster).

Silicic acid seems to be without influence upon phenolphthalein, for alkali silicates (the water-glasses) can be titrated with accuracy.

Chromic acid and acid chromates are changed by the addition of alkali to neutral chromates, which have no action upon phenolphthalein.

Alkali aluminates can be titrated accurately with this indicator, for aluminum hydroxide does not affect it.

Uses of Indicators. Indicators are used for two distinct purposes: (1) to show the actual concentrations of hydrogen ions in dilute solutions of acids and bases; and (2) to show the end point of a titration. The actual concentration of hydrogen ions depends upon the quantity of acid present and upon the extent to which the acid is ionized. A tenth-normal solution of acetic acid requires just as much sodium hydroxide to neutralize it as the same volume of tenth-normal hydrochloric acid, but the hydrochloric acid contains about 70 times as many hydrogen ions. The tenth-normal acetic acid has a pH value of about 2.9, and the hydrochloric acid a pH value of about 1. For many purposes it is

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[1] Alkaline-earth carbonates behave differently. They do not dissolve appreciably until the solution has a pH smaller than 6. Cf. p. 349.

much more important to know the pH value of a solution than the actual content of acid molecules.

The concentration of hydrogen ions, or the corresponding pH value, of a dilute solution of an acid or of a base can be computed easily from the so-called *ionization constant* of the acid or base. The ionization of a weak acid can be regarded as a chemical reaction that quickly reaches a state of equilibrium. Thus, if HA represents any weak acid, H^+ the hydrogen ion, and A^- the anion, the ionization reaction is
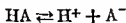
$$HA \rightleftharpoons H^+ + A^-$$

and the mass-action expression corresponding to this reaction is $[H^+] \times [A^-]/[HA] = k$. In such cases $[H^+]$, $[A^-]$, and $[HA]$ are usually expressed in moles per liter, and the concentrations are those corresponding to a state of equilibrium.

The stronger the acid, the larger the ionization constant. For a completely ionized acid, the ionization constant is assumed to be 1, cf. p. 461. The mass-action law does not help us much when the ionization is practically complete. When expressing concentrations in moles per liter we assume that one unit of a binary electrolyte gives two, and this leads to a mathematical error because the units are not absolutely the same. Such an error, however, can be disregarded in working with weak electrolytes

In considering the ionization of acids with more than one replaceable hydrogen, such as sulfuric or phosphoric acid, the ionization reactions should never be written $H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}$ or $H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{---}$ because the first equation states that one sulfate anion is formed for every two hydrogen ions and the second equation states that one phosphate is formed for every three hydrogen ions. This is false. The ionization of sulfuric acid takes place in two stages and of phosphoric acid in three stages.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \qquad\qquad H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$
$$HSO_4^- \rightleftharpoons H^+ + SO_4^{--} \qquad\qquad H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{--}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad HPO_4^{--} \rightleftharpoons H^+ + PO_4^{---}$$
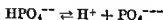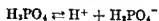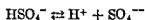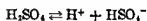
The corresponding mass-action expressions are

$$\frac{[H^+][HSO_4^-]}{[H_2SO_4]} = K_1 = [1] \qquad\qquad \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = K_1 = 1.1 \times 10^{-2}$$

$$\frac{[H^+][SO_4^{--}]}{[HSO_4^-]} = K_2 = 3 \times 10^{-2} \qquad\qquad \frac{[H^+][HPO_4^{--}]}{[H_2PO_4^-]} = K_2 = 2.0 \times 10^{-7}$$

$$\qquad\qquad\qquad\qquad\qquad\qquad \frac{[H^+][PO_4^{---}]}{[HPO_4^{--}]} = K_3 = 3.6 \times 10^{-13}$$

In the case of phosphoric acid, we may consider that three acids are present. The first, H_3PO_4, corresponds to a moderately strong acid and is about 35 per cent

ionized in tenth-normal solution; the second is weak and will not show an acid reaction to methyl orange; the third is an extremely weak acid. We can multiply the three equilibrium expressions together and get $\dfrac{[H^+]^3 \times [PO_4^{---}]}{[H_3PO_4]} = K_1 \times K_2 \times K_3$ $= 7.9 \times 10^{-22}$, which is precisely the same form of expression that we would get if the reaction $H_3PO_4 \rightarrow 3H^+ + PO_4^{---}$ took place, but in substituting numerical values we must remember that the quantities of H^+ formed by the secondary and tertiary ionization are inappreciable with respect to that formed by the primary ionization. The value of $[PO_4^{---}]$ would be merely that extremely low concentration formed by the tertiary ionization. The only significance of the expression $K_1 \times K_2 \times K_3$ is to show the effect that increasing the H^+ concentration has upon that of the PO_4^{---}. This explains, for example, why phosphates dissolve readily in solutions of HCl or HNO_3.

The following table shows the ionization constants of some acids and bases.

ACIDS		K_a	$p_a = -\log K_a$
Acetic		1.8×10^{-5}	4.74
Arsenic, K_1		5.0×10^{-3}	2.30
Benzoic		6.8×10^{-5}	4.16
Boric		6.0×10^{-10}	9.22
Carbonic	K_1	4.9×10^{-7}	6.31
	K_2	6.3×10^{-11}	10.20
Chromic, K_1		6.0×10^{-7}	6.22
Citric	K_1	8.0×10^{-4}	3.10
	K_2	5.0×10^{-5}	4.30
	K_3	2.0×10^{-6}	5.70
Formic		2.0×10^{-4}	3.70
Hydrogen cyanide		7×10^{-10}	9.14
Hydrogen sulfide	K_1	9×10^{-8}	7.05
	K_2	1.2×10^{-15}	14.92
Oxalic	K_1	3.8×10^{-2}	1.42
	K_2	3.5×10^{-5}	4.46
Phosphoric	K_1	1.1×10^{-2}	1.96
	K_2	2.0×10^{-7}	6.70
	K_3	3.6×10^{-13}	12.44
Sulfuric, K_2		3.0×10^{-2}	1.52
Sulfurous	K_1	1.7×10^{-2}	1.77
	K_2	1.0×10^{-7}	7.00
Tartaric	K_1	9.7×10^{-4}	3.01
	K_2	9.0×10^{-5}	4.05
Trichloroacetic		1.3×10^{-1}	0.88
BASES		K_b	$p_b = -\log K_b$
Ammonia		1.75×10^{-5}	4.76
Barium hydroxide, K_2		3×10^{-2}	1.52
Ethylamine		5.6×10^{-4}	3.25
Hydrazine		3.0×10^{-6}	5.52

Choice of Indicators in Titrations. The titration of an acid with a solution of a base is generally called a neutralization, but a sharp end point is obtained at pH = 7 only when the acid and base are both strong

electrolytes.   If the acid and base are equally strong, the end point with a weak acid and a weak base should occur at pH ~ 7 but it will not be sharp. This is illustrated by the plotted curves on p. 461. The titration of a weak acid with a weak base should be avoided whenever possible because of this difficulty in getting a sharp end point.

The curve on p. 461 for the titration of hydrochloric acid with sodium hydroxide shows that the titration is practically finished at about pH ~ 3.5 and the next drop of 0.1 N sodium hydroxide solution changes the pH to about 10.5. In reading such a curve, the true end point is taken as halfway up the nearly vertical line, which is at pH ~ 7 in this case. Any indicator that changes color between pH ~ 3.5 and pH ~ 10.5 should give a good result.

The curve for the titration of acetic acid with sodium hydroxide shows that the end point is at about pH ~ 9. Such a solution is alkaline because of the hydrolysis of sodium acetate. In this titration, therefore, the end point is not at the neutral point but at the *equivalence point*, i.e., it occurs when a quantity of sodium hydroxide *equivalent* to the acetic acid present has been added.   A study of the curve on p. 461 shows that methyl orange which changes color at pH ~ 2 to 4.0 is absolutely useless for this titration, but phenolphthalein which changes color at pH ~ 8.3–10 should give a good result.   A similar study of the titration of ammonia with hydrochloric acid will show that phenolphthalein is useless and that methyl red or methyl orange can be used. From the known values of water and the ionization constant of the weak acid or base titrated, it is possible to compute the pH value of the solution at the equivalence point, and when this is known the proper indicator can be chosen.

The hydrolysis of a salt can be expressed as follows:

$$ BA + H_2O \rightleftharpoons BOH + HA $$

when BA represents the formula of the salt, BOH that of the base, and HA that of the acid. Since most salts, excepting the halides of the highly ionized alkalies, are completely ionized in dilute aqueous solutions, this hydrolysis equation becomes:

$$ A^- + H_2O \rightleftharpoons OH^- + HA \qquad (1) $$

when BOH is a strong electrolyte and HA is a weak acid. The law of mass action is applied to this reaction of hydrolysis, and with the symbol K_h:

$$ \frac{[OH^-] \times [HA]}{[A^-]} = K_h \qquad (2) $$

The quantity of water involved in the reaction is very small in comparison with the total quantity of water in the solution so that $[H_2O]$ is regarded as a constant quantity and is left out of the mass action expression.

Now, if we multiply equation 2 by $\frac{[H^+]}{[H^+]}$,

$$\frac{[H^+] \times [OH^-] \times [HA]}{[H^+] \times [A^-]} = \frac{K_w}{K_a} = K_h \qquad (3)$$

Now according to equation 1 equal quantities of OH^- and HA are formed by the hydrolysis so that in equation 2 we can replace $[HA]$ with $[OH^-]$, and since the salt formed is practically completely ionized, we can replace $[A^-]$ with c, the concentration of the salt present in the solution. This gives us

$$\frac{[OH^-]^2}{c} = \frac{K_w}{K_a} = K_h \qquad (4)$$

and

$$[OH^-] = \sqrt{\frac{K_w}{K_a} \cdot c}$$

Using logarithms we have

$$\log [OH^-] = \tfrac{1}{2} \log K_w + \tfrac{1}{2} \log c - \tfrac{1}{2} \log K_a$$
$$= -7 + \tfrac{1}{2} \log c + \tfrac{1}{2} p_a.$$

because $\log K_w = -14$ and $-\log K_a = p_a$.

Then, by changing all the signs, the equation becomes

$$-\log [OH^-] = pOH = 7 - \tfrac{1}{2} \log c - \tfrac{1}{2} p_a$$

and since, according to p. 458, $pH + pOH = 14$, and $pH = 14 - pOH$, the formula for computing pH at the equivalence point in titrating *a weak acid with a strong base* is

$$pH = 7 + \tfrac{1}{2} \log c + \tfrac{1}{2} p_a.$$

Precisely the same line of reasoning leads us to the formula for the equivalence point in the titration of *a weak base with a strong acid*

$$pH = 7 - \tfrac{1}{2} \log c - \tfrac{1}{2} p_b.$$

The values for p_a and p_b are given for a few acids on p. 474. These last two equations enable one to choose the proper indicator for the titration of a weak acid or a weak base of which the ionization constant is known.

The indicator chosen should change color at the pH indicated for the equivalence point.

It is sometimes possible to titrate a mixture of two acids in such a way that the quantity of each acid present is known. This is accomplished by using two indicators. With equal initial concentrations of the two acids it is possible to titrate each separately with an accuracy of less than 1 per cent if the ionization constants are to one another as 10,000:1, or, in other words, if the difference in the ionization constants is at least 10^{-4}. If there is 100 times as much of one as of the other, there must be a difference of 10^6 in the constants. Thus it is possible to titrate hydrochloric acid in the presence of *boric acid* or *hydrochloric acid in the presence of acetic acid*. In the same way it is possible to titrate *carbonate in the presence of bicarbonate*; the two ionization constants of carbonic acid are 4.9×10^{-7} and 6.3×10^{-11}, respectively. Phenolphthalein shows when the carbonate is converted into bicarbonate, and methyl orange shows when all the bicarbonate has reacted with a strong

acid like hydrochloric. The ionization constants of phosphoric acid are $K_1 = 1.1 \times 10^{-2}$, $K_2 = 2.0 \times 10^{-7}$, and $K_3 = 3.6 \times 10^{-11}$. Methyl orange shows when the first end point is reached, and phenolphthalein indicates the second. An indicator changing at pH $12 - 14$ (trinitrobenzene) will give a fair idea of when the third hydrogen has all reacted, but the end point is not sharp.

Brönsted Definition of Acid and Base. Since the adoption of the ionization theory of Arrhenius in 1887, acids have been defined as substances which furnish hydrogen ions in aqueous solutions and bases as substances which yield hydroxide ions. In accordance with this conception, the neutralization of a dilute solution of acid by a base is expressed by the equation: $H^+ + OH^- \rightarrow H_2O$.

It has been known, for a long time, that the H^+ ions are not simply positively charged hydrogen atoms, or protons, but are hydrated just as most ions are. Under the Brönsted conception special emphasis is placed upon the fact that these hydrogen ions are hydrated; they are given the symbol H_3O^+ and called *hydronium* ions, *hydroxonium* ions, or *oxonium* ions by advocates of the system.

Brönsted's definition is based on the assumption that any substance can be considered as acid if it can lose a proton. A base is a substance which can accept a proton. Water acts as a base when it unites with a proton to form H_2O. When a compound behaves as an acid, it is transformed into its corresponding *conjugate base* as illustrated by the equation

$$A \rightleftharpoons B^- + H^+$$
$$\text{acid} \quad \text{base} \quad \text{proton}$$
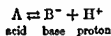
Since free protons are not present in solution, a dissolved acid will dissociate electrolytically only when the solvent can accept protons and act as a base. Just as water acts as a base to form H_3O^+ ions, so NH_4^+ ions dissolved in liquid ammonia have chemical properties which we regard as acidic.

In dealing with aqueous solutions, little is to be gained by the Brönsted formulation of acid-base equilibria with water. The mathematical treatment is essentially the same as when the Brönsted theory is not used. The chief points of difference are the substitution of *hydronium* ion for *hydrogen* ion and the change in the definition of acids and bases. Sodium carbonate is a salt in the older system, but the carbonate ion is a *base* according to Brönsted. We have always known, however, that the anions of compounds like Na_2CO_3 and $NaC_2H_3O_2$ have basic properties with respect to neutralizing acids, and Na_2CO_3 has been used to standardize solutions of acids ever since the early days of the nineteenth century. The Brönsted nomenclature is used by many modern writers who like to think of water, NH_3, $C_2H_3O_2^-$, CO_3^{--} as bases when they unite with H^+ ions to form H_2O, undissociated acetic acid, carbonic acid, etc. When, in this book, we speak of hydrogen ions and write the symbol H^+, we do so with the full realization that these ions are hydrated just as copper ions and most other ions are. The Brönsted terminology is somewhat more complicated than that of the older and more conventional system. A student brought up entirely on this newer nomenclature will be confused by many statements in current literature and in the older writings.

The titration of borax with hydrochloric acid can be used as an example of the different ways in which the underlying chemical reaction can be explained. Borax, according to the older nomenclature, is a salt of a strong base (NaOH) and a very weak acid (H_3BO_3). Borax dissolves in water but the acid is so weak that hydrolysis takes place to a considerable extent because boric acid is so weak that the $B_4O_7^{--}$ ions react with the H^+ ions of water to form H_3BO_3.

$$B_4O_7^{--} + 7H_2O \rightarrow 4H_3BO_3 + 2OH^-$$
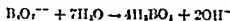
and added H^+ ions react with the OH^- ions to form H_2O so that the final reaction results in the complete conversion of all $B_4O_7^{--}$ ions to H_3BO_3,

$$B_4O_7^{--} + 2H^+ + 5H_2O \rightarrow 4H_3BO_3$$
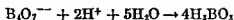
According to the Brönsted nomenclature, the $B_4O_7^{--}$ ion is what is called a *conjugate base* and reacts with H_3O^+ ions as follows:

$$B_4O_7^{--} + 2H_3O^+ + 3H_2O \rightarrow 4H_3BO_3$$
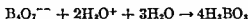
There is little to choose between the two explanations because the fundamental fact to be explained in both cases is that an aqueous solution of $Na_2B_4O_7$, with methyl red as indicator, can be titrated according to the equation

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3$$

Titration of 0.5 N Solutions of HCl and NaOH

To prepare 1 l of 0.5 N HCl, measure out approximately $0.5 \div 0.012 = 41.7$ ml of 12 N HCl or 83.3 ml of 6 N HCl and dilute to approximately 1 l. Since the solution is to be standardized, it is unnecessary to measure the acid or the water accurately. Pour the acid into an ordinary glass-stoppered quart bottle, and fill with water up to about 2 in. from the bottom of the neck. It is important that enough empty space is left to permit thorough mixing by shaking. Stopper the bottle and shake for at least 2 minutes.

Prepare 1 l of 0.5 N sodium hydroxide by weighing out on the laboratory scales about 20 g of solid sodium hydroxide. Dilute with distilled water to about 1 l, and mix by shaking at least 2 minutes. Since this basic solution attacks glass slightly and sodium silicate is a good cementing agent, it is well to use a rubber stopper in the bottle and unwise to use the solution in a glass-stoppered buret.

Solutions of alkali hydroxide attack glass to form Na_2SiO_3. The reaction takes place slowly but becomes appreciable on standing. It is well to heat the empty bottle carefully to about 100° on the outside, place a piece of paraffin in it, and rotate until the inside of the bottle is thinly coated with paraffin. Solutions of acid also attack glass slightly on standing.

After the solutions are once mixed, the concentrations will remain uniform as a result of the osmotic pressure of the solutes, but there is always a slight loss by evaporation if the bottle is not kept stoppered. If a warm day is followed by a cool night there is likely to be some condensed moisture on the sides of the bottle so that it is always well to give the contents of the bottle a slight shaking every time a fresh portion is taken.

Take a plain buret that has been thoroughly cleaned with chromic acid

solution (cf. p. 438) and washed with water. Never allow it to remain empty for any length of time; a buret that has been dry for some time will rarely drain well. When the buret is not in use, fill it with water, or with the solution which is used in it, and cap it with an inverted test tube. Rinse the buret with three 10-ml portions of the sodium hydroxide solution, emptying it each time. Discard the solution thus used. Fill the buret to slightly above the graduations, make sure that there is no entrapped air bubble in the rubber tubing at the bottom of the buret, which must be full of liquid, and then drain out the solution until the bottom of the meniscus at the upper level is exactly at 0.00 or slightly below. To remove entrapped air, bend the flexible tubing so that the tip points upward and allow a little solution to run out. In filling a buret, pour the reagent directly from the bottle into the buret. The use of a funnel or small beaker is likely to lead to error. In the same way, rinse out a carefully cleaned, glass-stoppered buret with water and with three separate portions of the 0.5 N acid, and fill to approximately the zero mark. Make sure that the bottom of the stopper is filled with liquid. Read each buret to the nearest 0.01 ml, and record the readings in the notebook (cf. p. 439 with respect to the use of blue, glazed paper). Measure out about 40 ml of the alkali hydroxide solution into a 200-ml Erlenmeyer flask, dilute with 50 ml of water, add 2 drops of methyl orange indicator solution and titrate with the acid until the solution *begins* to change from yellow to pink. As a rule a little too much acid will be added at first; if this happens, add a little more of the sodium hydroxide to turn the color back to a distinct yellow. Then add the acid very carefully until the well-stirred solution assumes a pink tint. Read each buret again.

Refill the burets and repeat the titration in the same way. Record the readings and compute the relative strengths according to the following scheme, which represents a sample page of a notebook.

TITRATION OF HCl vs. NaOH. OCT. 3, 1941

Determination	I	II
Final reading HCl............	48.08	43.14
Initial reading HCl...........	0.12	0.17
	47.96	42.97
Final reading NaOH.........	46.29	40.37
Initial reading NaOH........	1.75	0.50
	44.54	39.87
log ml HCl.................	1.6808	1.6332
log ml NaOH................	1.6488	1.6007
	0.0320	0.0325*
1 ml of NaOH neutralizes......	1.076	1.077 ml HCl

* In titrations of one solution against another and in standardizations, the logarithms of the final values should agree within 0 0003. This corresponds to a check in the values of 2 parts in 1000. If necessary, repeat the work until this agreement is obtained.

The above procedure was made with a back titration. Sometimes it is advantageous to titrate to a *dead stop* end point. To do this in the titration of base with acid, keep the contents of the flask in constant motion, and, when a color change is apparent, close the buret and keep swirling the solution until the original yellow color is restored. Now add the acid more slowly, and, as the end point is approached, finally add the reagent dropwise, making sure that the yellow color is restored before adding a fresh drop. It is well to have for comparison a like volume of water containing the same quantity of indicator and a tiny drop of acid (0 02 ml) and end the titration when the two colors match. With a little practice, this *dead stop* end point can be determined as quickly and as accurately by this method as when a back titration is necessary because a slight excess of reagent was added.

Standardization of Acids and Bases

There are many excellent ways in which a solution of hydrochloric acid can be standardized with satisfactory accuracy. The standardization can be accomplished gravimetrically by taking a measured volume of the acid from a pipet or buret, diluting with water, adding a slight excess of silver nitrate, heating to coagulate the precipitate, filtering, and weighing the silver chloride precipitate. Such a procedure corresponds to the determination of chlorine in a sample of sodium chloride.

The acid solution can be standardized by measuring the volume required to react with a pure substance of definitely known chemical composition. A satisfactory standard is sodium carbonate prepared by heating pure sodium bicarbonate to 270°. Gay-Lussac recommended this method early in the nineteenth century. Other standards which have given good results are: calcite (Grandeau and also Pincus in 1863); potassium bicarbonate (Ure, 1839); sodium bicarbonate (North and Blakey, 1905); potassium bitartrate (Borntraeger, 1892), which is first converted into potassium carbonate by heating strongly; sodium oxalate (Sörenson, 1893), which is converted into sodium carbonate by ignition; and borax (Salzer and also Rimbach in 1893). Frequently it is convenient to standardize the acid against a solution or

base which has itself been standardized. This last procedure is called the *indirect method.*

There is no good gravimetric method for standardizing a solution of sodium hydroxide, but numerous pure substances have been recommended as standards. Pure oxalic acid crystals, $H_2C_2O_4 \cdot 2H_2O$, were used by Fr Mohr in 1852, and since then the following are only a few of the acids or acid salts which have been advocated: potassium acid oxalate, KHC_2O_4; potassium tetroxalate, $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$; succinic acid, $C_2H_4(CO_2H)_2$; potassium biiodate, $KH(IO_3)_2$; benzoic acid, $C_6H_5CO_2H$; potassium acid phthalate, $KHC_8H_4O_4$ An indirect method of standardizing sodium hydroxide solution is the titration against a solution of acid which has been standardized.

Standardization of Acid against Sodium Carbonate, Na_2CO_3

Preparation of the Standard. If pure sodium bicarbonate is not available, dissolve about 35 g of the commercial product in 350 ml of warm water and filter off any insoluble residue. Allow the water to evaporate slowly at a temperature not above 40° until about 25 g of salt has deposited. Protect the solution from contamination by dust by covering it with a watch glass supported upon a glass triangle or glass supports. Finally pour off the mother liquor; dry the crystals by pressing them between filter papers and by heating for an hour at 120°. Preserve the pure sodium bicarbonate in a glass-stoppered bottle.

Place about 8 g of pure sodium bicarbonate in a platinum or porcelain crucible and heat for 30 minutes at a temperature of about 270°, taking care that the temperature does not rise above 300°. The heating can take place in an electric oven, a sand bath, or an air bath.

If a sand bath is used, embed the crucible so that the sand on the outside is level with the sodium bicarbonate on the inside. Occasionally stir the contents of the crucible with a 360° thermometer. After heating the crucible for half an hour, allow it and its contents to cool in a desiccator over calcium chloride or other suitable desiccant. Preserve the sodium carbonate in a glass-stoppered weighing bottle. If exposed to the air or kept in a cork-stoppered bottle it soon absorbs water from the atmosphere and becomes worthless as a standard.

Standardization. To standardize 0.5 N hydrochloric acid, weigh out two separate portions of about 1 g of sodium carbonate and record the weight to the nearest tenth of a milligram. The best way to do this is to place a little more than 2 g of the standard in a glass-stoppered weighing tube. Weigh this tube and its contents and record the weight after counting the missing places in the box of weights. Check this value by counting the weights on the pan. Every student is likely to make a mistake in recording a weight, but he will almost always notice the mistake if he habitually checks his observations. Take the weighed

green. In the case of the $KH(IO_3)_2$ the standardization is based on the reaction

$$H(IO_3)_2^- + 11H^+ + 10I^- \rightarrow 6I_2 + 6H_2O \text{ and } eleven \text{ moles of } H^+ \text{ are neutralized.}$$

Potassium biiodate (also called potassium acid iodate or potassium hydrogen iodate) is a fairly strong acid with ionization constant 1.9×10^{-1}. It can be used, therefore, for the direct standardization of alkali hydroxide solutions, and, since it can be obtained very pure, it can be regarded as one of the most useful standards for acids, bases, or sodium thiosulfate (see "Iodimetry"). In the absence of iodide, the equivalent weight is 195.0.

Mercuric oxide, HgO (equivalent weight 108.3), has also been recommended The weighed oxide is dissolved in an excess of KI solution, and the liberated OH^- is titrated with an acid in the presence of an indicator that changes color between pH 8 and 4.

$$HgO + 4I^- + H_2O \rightarrow HgI_4^{--} + 2OH^-$$
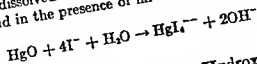
Standardization of Sodium Hydroxide

(a) With Potassium Acid Phthalate, $KHC_8H_4O_4$

This substance, because of its high molecular weight, is particularly well suited for the standardization of dilute solutions of sodium hydroxide. To standardize 0.1 N sodium hydroxide, about 1 g of the salt should be taken, as this is sufficient to neutralize 49 ml of the base. Phenolphthalein is a suitable indicator, but reliable results cannot be obtained with methyl orange. The chief difficulty that students have in working with phenolphthalein arises from the fact that the sodium hydroxide absorbs a little carbon dioxide from the air every time the storage bottle is opened, unless care is taken to prevent it. This can be accomplished by pumping the sodium hydroxide into the buret, or by siphoning it from the storage bottle, in such a way that all air that enters the bottle has to pass through a tube containing soda-lime $(Ca(OH)_2 + NaOH)$ or Ascarite (a patented preparation of asbestos fibers impregnated with sodium hydroxide). Keeping the solution under a layer of gasoline is effective also. Every molecule of carbon dioxide that combines with two molecules of sodium hydroxide to form sodium carbonate yields a product that reacts only with one molecule of hydrogen chloride in the cold because the sodium bicarbonate, which is formed when one molecule of hydrochloric acid acts on one molecule sodium carbonate, is neutral to phenolphthalein. The resulting error can be overcome by boiling the acid solution of the neutralized solution to expel carbon dioxide and repeating the process if the phenolphthalein color has been determined with methyl orange as indicator. If the ratio of acid to base has been determined with methyl orange as indicator, the presence of carbonate in the sodium hydroxide will be detected by determining the ratio with phenolphthalein. The sodium hydroxide solution will prove weaker when phenolphthalein is used if it contains carbonate and the titration is carried out in the cold.

Procedure. To standardize 0.5 N sodium hydroxide, weigh out 2.5- to 3.0-g portions of potassium acid phthalate into 200-ml Erlenmeyer flasks. Record the weights to the nearest milligram. Add 100 ml of water to each portion and shake gently until all the solid has dissolved. Add 3 drops of phenolphthalein solution and titrate till a pale pink color is obtained. Heat the solution to boiling; if the color

fades, add more of the sodium hydroxide solution until the color persists after boiling for 30 seconds. Record the data as shown on p. 482. The equivalent weight of potassium acid phthalate is the molecular weight, 204.1. Compute the normal concentration of the base, and, from the ratio of acid to base previously found, compute the normal concentration of the hydrochloric acid solution as well.

For the most accurate work, the solution of sodium hydroxide must be prepared free from carbonate, the water used for dissolving the standard must have been recently boiled to remove carbon dioxide, the titration must take place in a flask which has been swept free from carbon dioxide by passing through it a stream of air that has been made to flow through granular soda-lime or Ascarite, and a blank test must be run under the same conditions to see how much sodium hydroxide would have been used if no potassium acid phthalate had been present. The volume used in the blank test must be deducted from that used in the standardization.

(b) With Benzoic Acid

Weigh out 1.5- to 2.0-g portions of the pure acid into 200-ml flasks, and record the weights to the nearest milligram. Add 40 ml of alcohol, stopper the flask, and allow to stand until all the acid has dissolved. Add 3 drops of phenolphthalein indicator, dilute with water to 100 ml, and titrate with the 0.5 N sodium hydroxide. When a slight pink color is obtained, heat the solution and see if the color disappears. If so, add more sodium hydroxide until the color is not bleached by boiling for 30 seconds. Run a blank test with the same quantities of water and alcohol, and deduct the volume of sodium hydroxide required in this test from the total volume used in the standardization.

Everything that was said under (a) concerning the effect of carbon dioxide is true here. Sodium hydroxide free from carbonate can be prepared by adding about 20 ml of 0.5 N barium chloride to the sodium hydroxide solution. Allow the precipitate of barium carbonate to settle; stopper the bottle with a two-hole rubber stopper carrying a short right-angled tube attached to a soda-lime tube through which air can enter the bottle and also carrying a siphon tube reaching nearly to the bottom of the bottle. Then place the bottle on a shelf above the buret and siphon the solution into the buret as required. See Fig. 81. The valve at a is made by a round bead in the rubber tubing.
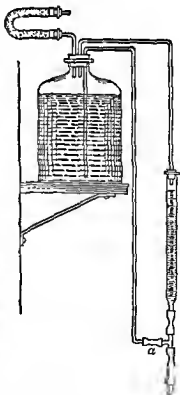
Fig. 81.

(c) With Constant-Boiling Hydrochloric Acid[1]

Set up a distilling apparatus with a liter flask and a water-cooled condenser. Place in the flask about 750 ml of approximately 6 N HCl and distil at the rate of 3–4 ml per minute. After about three-quarters of the original liquid has been distilled and rejected, collect the constant-boiling acid in a dry flask. Continue distilling until only 50–60 ml of liquid remains in the distilling flask. Preserve in a glass-stoppered bottle. Read the barometer to the nearest millimeter. The exact composition of the liquid varies slightly with the barometric pressure that prevails during the distillation, as the following table shows.

ATMOSPHERIC PRESSURE IN MILLIMETERS OF MERCURY	WEIGHT OF HCl IN 1 g OF DISTILLATE	MILLIEQUIVALENTS PER GRAM OF DISTILLATE
780	0.2018	5.536
770	0.2020	5.543
760	0.2023	5.550
750	0.2026	5.556
740	0.2028	5.563
730	0.2030	5.569

Each millimeter difference in barometric pressure corresponds to about 0.02 mg in the actual HCl content of 1 g of the acid. The value for any intermediate pressure can be interpolated with an accuracy of 1 part per 1000 or better.

To use the acid for standardizing 0.5 N NaOH, weigh a clean and dry glass-stoppered weighing tube to the nearest 0.1 mg, add 3–4 ml of the constant-boiling acid, weigh the tube again, and transfer to a 200-ml Erlenmeyer flask by washing the tube thoroughly with a stream of water from a wash bottle. Dilute to about 100 ml, add methyl red or methyl orange indicator solution, and titrate to the color change.

The acid can also be weighed from a weight buret such as that shown in Fig. 79, p. 446. It can be used for preparing standard solutions by diluting a weighed portion to the mark in a volumetric flask and mixing.

Normal Hydrochloric Acid
1000 ml contains 36.47 g of HCl

Dilute pure, concentrated hydrochloric acid of the laboratory with 11 volumes of water. In this way a solution is obtained that is slightly more than normal in strength. To obtain an exactly normal solution, titrate it against a weighed amount of chemically pure sodium car-

[1] Foulk and Hollingsworth, *J. Am. Chem. Soc.*, **45**, 1220 (1923); Hulett and Bonner, *ibid.*, **31**, 390 (1909); Bonner and Branting, *ibid.*, **48**, 3093 (1926).

bonate, and from the result obtained compute the volume of water to be added. Constant-boiling hydrochloric acid can be used more advantageously (see p. 486).

In the standardization of any volumetric solution it is advisable to take a weight of substance such that the titration can be accomplished with one filling of the 50-ml buret and heavy enough so that the normal titration error will not amount to more than 0.001 of the total volume of standard solution used. This is accomplished by taking enough substance to react with 35–40 ml of the solution to be standardized. It is always well to run a blank with the water used, to see how much of the solution is required to give an end point similar to that used in the analysis. The blank titration should have the same volume of water, the same amount of indicator, and the same temperature as the main solution, and in working with methyl orange it is best to match the shades.

To standardize the acid, proceed as directed on pp. 481–484. Of pure sodium carbonate, use about 2 g for a normal solution; add 100 ml of water and 2 drops of methyl orange indicator solution. Start the titration at approximately the zero reading of the buret. Record the reading in the notebook, estimating to the nearest hundredth of a milliliter. Titrate slowly with constant stirring until the color changes from yellow to orange. With a little practice it is easy to tell when the end point is nearly reached by the fact that a pink color is produced which fades slowly on stirring. Finally, at the right end point, the color changes from yellow to orange throughout solution. It is advisable to match the color with that obtained by adding the indicator solution to pure water and adding just enough acid to give an orange tint to the solution.

If the end point is overstepped, add enough standard sodium hydroxide (p. 489) to restore the yellow color and finish with acid again. Titrate the sodium hydroxide against the acid as described on p. 479.

Computation. If no sodium hydroxide is used the computation is very simple. By definition, 1 ml of normal acid reacts with 1 milliequivalent of sodium carbonate (molecular weight 106 05), or 0 05303 g of Na_2CO_3. To find the ratio to the normal, or normality of the acid, it is only necessary to find out how much sodium carbonate was actually neutralized by 1 ml of the acid and divide this value by the milliequivalent, or norm, of sodium carbonate

Thus if t ml of acid was required to neutralize s g of sodium carbonate, the solution is $\dfrac{s}{t \times 0\,05303}$ normal.

If the end point was overstepped it is necessary to know the relative strengths of the acid and base used in the titration Assume that by titration it was found that a ml of HCl = b ml of NaOH.

Then 1 ml NaOH = $\frac{a}{b}$ ml of HCl. If, in the titration of s g of sodium carbonate, p ml of HCl and q ml of NaOH were used then $t = p - \frac{a}{b} q$ and the above equation holds. If N_A is the normality of the acid, $N_A' \times \frac{a}{b} = N_B$, the normality of the sodium hydroxide.

When many analyses have to be made as a part of the routine work of a commercial laboratory it is convenient to make the solutions of acid and base of exactly the same strength and to keep the solutions always exactly normal, or 0.1 N, or 0.5 N as the case may be. Since it is not practical to concentrate a large volume of solution to a definite volume by evaporation it is advisable to make up the solution so that it is a little stronger than desired. If N is the desired normality and N' the normality of the solution as first made up, then the solution is $\frac{N'}{N}$ as strong as desired and should be diluted accordingly.

Thus if the solution is 1.023 N it is only necessary to add 23 ml of water to each liter of solution to make it 1 N; if it is 0.5012 N, add 1.2 ml of water to each 500 ml of solution to make it exactly 0.5 N. Measure out the solution in a measuring flask calibrated for delivery and add the required volume of water from a buret.

Place a label on each standard reagent and write on it the normal concentration with 4 significant figures and the date that the standardization was made. This is desirable because solutions often change on standing as a result of evaporation, of the action of the reagent on the glass container, or of decomposition as a result of impurities present.

For most purposes a normal solution is too strong, and 0.1 or 0.5 N solutions are more commonly used. Prepare these exactly the same way but by using correspondingly smaller quantities of reagents. In titrating with 0.1 N solutions it is quite necessary to make allowance for the acid or base required to react with the indicator and important to keep all conditions the same, such as temperature, volume, and quantity of indicator used in duplicate titrations. Alkaline solutions should not be used in burets with a glass stopcock.

All volumetric titrations should be carried out in duplicate. Burets should be rinsed with at least three 10-ml portions of the liquid before being filled. They must be kept clean so that no drops form on the sides as they drain. In using measuring flasks they should also be well cleaned (see p. 437), and when used as above, they should be rinsed with at least three 25-ml portions of the liquid before being filled.

Normal Nitric and Sulfuric Acid Solutions

These are prepared in the same way as was described in the preparation of normal hydrochloric acid.

0.1 N Oxalic Acid

$$1000 \text{ ml contains } \frac{H_2C_2O_4 \cdot 2H_2O}{20} = \frac{126.06}{20} = 6.303 \text{ g}$$

An oxalic acid solution of this strength can be prepared by dissolving exactly 6.303 g of pure, crystallized oxalic acid in water and diluting

to a volume of 1 l in a calibrated flask with water at the laboratory temperature (cf. p. 453). Titration with this acid should be made with phenolphthalein as indicator.

Normal Sodium Hydroxide Solution
1000 ml contains 1 NaOH = 40.01 g

Dissolve about 45 g of commercial caustic soda in a little more than a liter of water. Allow the solution to stand for about 1 hour beside the hydrochloric acid against which it is to be titrated, in order that both solutions may be at the same temperature. Measure off about 40 ml of the solution from a buret, and titrate with normal hydrochloric acid after the addition of 2 drops of methyl orange solution. The necessary computation was indicated on p. 455. The solution can be standardized directly (p. 484).

Titration of Alkali Containing Carbonate with Phenolphthalein in Hot Solutions

To the alkaline solution introduce 2 drops of phenolphthalein indicator and add, from the buret, hydrochloric acid of approximately the same strength until the red color disappears. Heat the solution to boiling; the red color soon reappears. Cool by placing the beaker in cold water,[1] again decolorize with hydrochloric acid, and repeat the process until finally the red color does not reappear on boiling. This method of titration is tedious, but the results obtained are accurate.

On titrating 0.1 N acids with methyl orange as indicator, there is no sharp change from yellow to pink, as with normal and half-normal solutions, but first a brownish orange color is obtained which becomes pink on the addition of more acid. The correct end point is the change from yellow to yellowish brown. Only when considerable carbonate is present will this change occur before enough acid has been added, for in this case the carbon dioxide exerts an action upon the methyl orange. The disturbing action of carbon dioxide is best prevented by first titrating in the cold, then heating to remove the carbon dioxide, again titrating the *cold* solution with acid. If only a small amount of carbonate is present, it exerts no appreciable effect upon methyl orange.

The titration of oxalic acid with alkali hydroxide solution which contains carbonate is best effected with phenolphthalein in hot solution. The process is carried out as follows: Measure out about 40 ml of the sodium hydroxide into a beaker, add 2 drops of phenolphthalein, and

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[1] With phenolphthalein the titration can be finished in the hot solution, but the end point is not so sharp.

run in oxalic acid from a buret until the solution is decolorized. Heat the solution upon the water bath until the red color reappears, decolorize with oxalic acid, and continue the process until finally the color does not reappear on heating the solution. This point is reached, however, only after the solution has been evaporated to dryness and the residue taken up with a few milliliters of distilled water. A slight red color will appear after this first evaporation, but it will be discharged by the fraction of a drop of oxalic acid and will not reappear upon a second evaporation.

Remark. By heating the solution of oxalic acid over a free flame there is likely to be some decomposition. Sorensen thought that the trouble was caused by the following hydrolysis, $2Na_2C_2O_4 + H_2O = Na_2CO_3 + 2HCO_3Na + CO_2$, but Treadwell showed that the following reaction takes place when the sides of the containing vessel are overheated, $Na_2C_2O_4 = Na_2CO_3 + CO$.

Preparation of Sodium Hydroxide Solution Free from Carbonate

This is best effected as proposed by Küster.[1] Place about 40 ml of pure alcohol in a small round-bottomed flask, heat to boiling on the water bath, and add little by little 2.5 g of bright metallic sodium, freed from petroleum by rubbing between pieces of blotting paper. The reaction between the boiling alcohol and the sodium is at first very violent, and large amounts of hydrogen and alcohol vapors are evolved. During this time keep the flask covered with a watch glass. Gradually the reaction begins to diminish and finally stops. In the flask there will be a deposit of sodium alcoholate and some undissolved sodium on account of the insufficient amount of alcohol. Add small quantities of water free from carbon dioxide,[2] a test tube full at a time. Boil off most of the alcohol and, in order to remove it completely, pass a current of air free from carbon dioxide through the solution until the odor of alcohol can no longer be detected. Cool quickly, adding cold water free from carbon dioxide; immediately place in a liter flask, and dilute to the mark with pure water at 17–18°. This solution will give the same value when titrated with cold or with hot phenolphthalein.[3] With methyl orange correct results are obtained cold if the orange color is taken as the end point.

Such a solution quickly absorbs carbon dioxide from the air. In order to prevent this, place it in a bottle as shown in Fig. 81, p. 485,

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[1] Z. anorg. Chem., 13, 134 (cf. p. 485).

[2] Pass air, freed from carbon dioxide by a soda-lime tube, through the boiling water.

[3] Provided that the hydrochloric acid solution was prepared with water free from carbonate; otherwise too little acid will be necessary when the titration takes place in the cold.

which is connected with a soda-lime tube, N, and with the buret by means of the tubes p and r. The buret is filled through the valve at a. In this way a solution can be kept free from carbon dioxide for a long time. To determine whether the solution is free from carbonate, make two parallel titrations with phenolphthalein as an indicator, one in the cold and the other in the hot solution. If the results agree the solution is free from carbonate. Otherwise it is necessary to prepare a fresh solution or to make a corresponding correction in each analysis after determining the amount of carbonate present as described on p. 498.

In many cases it is better to use a 0.1 N barium hydroxide solution; as long as it remains clear it is free from carbonate.

Preparation of 0.1 N Barium Hydroxide Solution

$$1000 \text{ ml contains } \frac{Ba(OH)_2 + 8H_2O}{20} = \frac{315.51}{20} = 15.78 \text{ g}$$

The crystallized barium hydroxide of commerce always contains barium carbonate, so that the solution cannot be prepared by simply weighing out the necessary quantity and diluting to 1 l. Dissolve about 20 g of the commercial hydroxide in the necessary amount of distilled water within a large flask. Close the flask and shake until the crystals have completely disappeared and a light, insoluble powder of barium carbonate remains. Allow the solution to stand for 2 days, until the barium carbonate has completely settled; siphon it off into a bottle through which a current of air free from carbon dioxide has been passed for 2 hours previous. Connect this bottle with a soda-lime tube and with a buret as shown in Fig. 81, p. 485. For the titration, place 50 ml of 0.1 N hydrochloric acid in an Erlenmeyer flask, add a little phenolphthalein, and titrate with the barium hydroxide solution. The normality found should be written upon the label. It is not advisable to make the solution exactly 0.1 N, for it usually becomes turbid on diluting.

A. ALKALIMETRY

1. Determination of Alkali Hydroxides

Rule. If the substance to be analyzed is a solid, dissolve an accurately weighed quantity in enough water to make the solution of about the same concentration as that of the acid to be used in the titration. If a solution of an alkali hydroxide in water is to be analyzed, determine the specific gravity of the solution, then dilute accordingly.

(a) Determination of Sodium Hydroxide in Commercial Caustic Soda

For the titration 0.5 N hydrochloric acid solution can be used. As sodium hydroxide absorbs carbon dioxide from the air it is difficult to get a good sample. Place the material in a weighing beaker and weigh out a sample of 4–6 g into a liter measuring flask. Dissolve in water that has been freed from carbon dioxide (p. 490), and dilute the cold solution up to the mark. Mix, measure out 100-ml aliquot portions for the titration with methyl orange as indicator.

Computation. If 5.001 g were taken for analysis and in the titration of the aliquot 24.18 ml of 0.5 N acid were used, the percentage purity of the sample can be computed as follows:

1 ml of 0.5 N HCl = 0.02000 g NaOH (NaOH = 40.01)

Therefore,

$$\frac{24.18 \times 0.02000 \times 100}{0.5001} = 96.72 \text{ per cent NaOH}$$

In this particular case, note that the volume of HCl solution used is exactly one-fourth the percentage of pure NaOH present. This is because the weight of sample in the aliquot (0.5001 g) was 25 times the value of 1 ml of 0.5 N acid in terms of NaOH. The practice of using an original weight such that the final computation can be done mentally is very common in commercial work.

(b) Determination of Sodium Hydroxide Present in Caustic Soda Solution

Assume that caustic alkali solution of d 1.285 is to be analyzed. A table in the back of this book shows that the solution should contain 25.8 per cent of NaOH by weight. One milliliter of solution should contain 1.285 × 0.258 = 0.3315 g NaOH.

If it is desired to know the percentage by weight of sodium hydroxide (or its equivalent, as base) present, weigh out about 3 g of solution into a small beaker, add 50 ml of water, and titrate with 0.5 N acid, using methyl orange as indicator.

If it is desired to know the weight of NaOH per milliliter, measure out 25 ml of the caustic soda solution, dilute with water at the laboratory temperature to 1000 ml, mix, and use 100 ml for the titration.

Remark. The titration of alkali hydroxides with methyl orange as an indicator will only give correct results when the alkali hydroxide is free from carbonate, which with commercial material is never the case. The above results are too high, for

they represent the total amount of alkali, i.e., the amount of NaOH + Na$_2$CO$_3$, though the latter is expressed in terms of NaOH. For an accurate determination of alkali hydroxide in the presence of alkali carbonate, see p. 498.

(c) Determination of Ammonia in Aqueous Ammonia

The procedure is the same as under (b).

(d) Determination of Ammonia in Ammonium Salts

Weigh out 1 to 2 g of the ammonium salt in the flask K (Fig. 82, p. 494), dissolve in about 200 ml of water, and treat with 10 ml of a boiled solution of 10 per cent caustic soda. Distil until no more NH$_3$ is being evolved, as shown by testing 10 ml of the last distillate with litmus or turmeric paper, and receive the distillate in a known volume of 0.5 N acid in the receiver V or in a saturated solution of boric acid, as described on p. 494. In the latter case the boric acid prevents volatilization of NH$_3$ from the receiver but it is too weak an acid to affect the indicator in the following titration. Titrate the excess of acid with 0.5 N caustic alkali, in the presence of methyl orange or methyl red as an indicator if a known volume of mineral acid was used in the receiver, or titrate the ammonium borate with 0.5 N HCl if boric acid was used

Computation. 17.03 g of commercial ammonium sulfate was dissolved in 500 ml of water and one-tenth of the solution (1.703 g) placed in the flask. The distillate was caught in 60 ml of 0.5 N HCl and the excess of acid reacted with t ml of 0.5 N NaOH. Since the equivalent weight of NH$_3$ is 17.03 there is present

$$\frac{(60 - t)0.008515 \times 100}{1.703} = \frac{60 - t}{2} = \text{per cent NH}_3$$

Kjeldahl Method. The Kjeldahl method for determining nitrogen in organic substances consists in converting the nitrogen into ammonium acid sulfate while decomposing the organic matter with boiling sulfuric acid and some catalyzer. For student work when the class is large, a sample of blood meal mixed with flour is suitable for this analysis.

After the organic matter has been decomposed completely, the solution is made alkaline with sodium hydroxide, liberating ammonia which is distilled into a measured volume of standardized acid solution or into boric acid solution. The excess of the standardized acid is finally titrated with standard sodium hydroxide with methyl red as an indicator or the ammonium borate is titrated directly with standard acid (cf p. 469) One milliliter of normal acid neutralizes 0.014 g of nitrogen in the form of ammonia

The method has undergone much modification from time to time in order to include in the results which is not easily reduced to ammonia. Thus to include nitrogen present as nitrate it is customary to add 0.04 g of salicylic acid for each milliliter of concentrated sulfuric acid used

To test for nitrate in the presence of organic matter, heat a little of the sample with 10 ml of water. Place 1 ml of concentrated sulfuric acid in a porcelain crucible and dissolve in it 2–3 mg of carbazole (diphenylimide, $C_6H_4 \cdot NH \cdot C_6H_5$). Add, with stirring, a little of the aqueous solution to be tested for nitrate; a deep green color shows the presence of nitrate (disregard a slight coloration). If nitrate is present, digest the sample with 30 ml of concentrated sulfuric acid containing 1 g of salicylic acid. Mix by shaking, and allow to stand 30 minutes. Then add in small portions 5 g of powdered $Na_2S_2O_7 \cdot 5H_2O$ and heat 5 minutes. Cool under running water, add the catalyzers, and continue as in the absence of nitrate.

Procedure. Weigh out 0.35 to 3.5 g of finely ground substance into a 500-ml Kjeldahl flask,[1] add 10 g of powdered potassium sulfate, 0.2 g selenium, and 20 to 25 ml of concentrated sulfuric acid. Shake to mix the contents of the flask; place over a hole in an asbestos board on the ring of a lamp stand with the flask inclined at an angle of about 60°. Heat below the boiling point until there is no more frothing, adding a little paraffin wax if the frothing is violent. Take care to use a small

flame protected by the asbestos board so that the flame does not touch the flask except where the inside is wet with acid. Gradually increase the heat until the decomposition is complete and the solution is nearly colorless. Boil gently for about 30 minutes, allow to cool, and connect with another flask and a condenser through a splash trap as shown in Fig. 82. The flask on the right contains water from which steam is generated. When heated in this way the solution in the other flask can be boiled without bumping. The side-armed distilling flask shown between the flask and the condenser acts as an efficient splash trap and prevents any spray containing NaOH from being carried over mechanically into the receiver. In
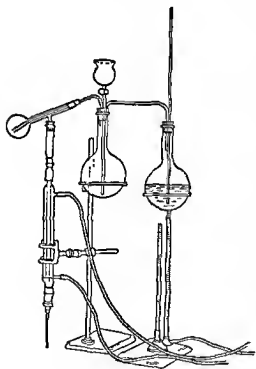
Fig. 82.

the receiver (a 250-ml Erlenmeyer flask) place 50 ml of 5 per cent boric acid solution. Dilute the H_2SO_4 solution with about 200 ml

[1] Kjeldahl flasks can be obtained which are suitable both for the original digestion with the acid and for the subsequent distillation. If a smaller Kjeldahl digestion flask is used, rinse the solution into a larger flask before adding the sodium hydroxide to make the solution alkaline.

of water, poured through the funnel of the flask, and add sufficient 12 N NaOH to make the solution basic (80 ml should be sufficient). Distil over about 150 ml of liquid by boiling the water in the flask shown on the right. This boiler should have a safety tube extending from the bottom of the flask to at least a foot above the neck. The boric acid in the receiver helps to retain the NH_3, but the acid is so weak that the ammonium borate formed titrates exactly as if it were free ammonia. After the distillation, remove the receiver, wash down the condenser tube, add the washings to the contents of the receiver, and titrate with standard HCl solution to a methyl red or better bromocresol purple end point. The equivalent weight of $N = 14$. $NH_3 + H^+ \rightarrow NH_4^+$ or

$$(NH_4)_2B_4O_7 + 2H^+ + 5H_2O \rightarrow 2NH_4^+ + 4H_3BO_3$$
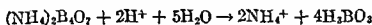
(e) Titration of Pyridine Bases[1]

1000 ml N acid = C_5H_5N = 79.05 g pyridine

The pyridine bases are so weak that they cannot be titrated with ordinary indicators. If, however, an aqueous pyridine solution is treated with an aqueous solution of ferric chloride, the iron is precipitated as ferric hydroxide:

$$FeCl_3 + 3C_5H_5N + 3HOH = 3(C_5H_5N, HCl) + Fe(OH)_3$$

If normal sulfuric acid is very carefully added with constant stirring until the precipitate redissolves, each milliliter of the acid required will correspond to $\dfrac{C_5H_5N}{1000} = 0.07905$ g pyridine.

Procedure. Dissolve 5 ml of pyridine in 100 ml of water, treat 25 ml of the resulting solution with 1 ml of 5 per cent aqueous ferric chloride solution, and titrate the precipitate of reddish brown ferric hydroxide with normal sulfuric acid until completely dissolved.

2. Determination of Alkali Carbonates

Alkali carbonates can be titrated in the cold by using methyl orange as an indicator, the end point being taken as the change from yellow to reddish orange. When fifth-, half-, and normal acids are used this is the correct end point, but with tenth-normal acids this change is obtained a little too soon, for large amounts of carbonic acid exert a slight action upon the indicator. In this case the difficulty is best overcome by titrating the solution until the orange color is obtained,

[1] K. E. Schulze, *Ber.*, **20**, 3391 (1887).

then heating to boiling to expel the carbon dioxide, cooling, and again titrating until the now yellow solution becomes orange again.[1] With phenolphthalein, accurate results may be obtained by titrating the hot solution (cf. p. 489). According to Warder,[2] sodium bicarbonate solution reacts neutral toward phenolphthalein in the cold, so that when a sample of sodium carbonate is titrated in the cold, with phenolphthalein as an indicator, an end point is obtained when the carbonate is changed to bicarbonate:[3]

$$Na_2CO_3 + HCl = NaCl + NaHCO_3$$
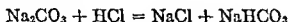
If the acid is allowed to run upon the carbonate solution, a part of the carbon dioxide from the sodium bicarbonate is likely to be lost, so that too much acid must be added before the end point is reached. On the other hand, correct results may be obtained if the titration is carried out slowly at 0° in the presence of NaCl (cf. p. 472) and with the solution gently and continuously stirred to prevent local concentration of the acid. This is important, for in this way a convenient method is obtained for determining the amount of hydroxide in the presence of carbonate.

Analysis of Soda Ash

Soda ash is the trade name for anhydrous sodium carbonate. The following procedure is applicable to the analysis of any alkali carbonate. It can also be used for an alkaline-earth carbonate but then it is necessary to add an excess of acid and titrate back with sodium hydroxide solution. As we have seen in the discussion of indicators, carbonic acid is such a weak acid that it has practically no effect upon methyl orange. The primary ionization of carbonic acid, however, furnishes hydrogen ions sufficient to make phenolphthalein assume its colorless form. With methyl orange as indicator, sodium carbonate, Na_2CO_3, can be titrated as if it were two molecules of sodium hydroxide, both stages of the following decomposition taking place before the solution is acid to methyl orange:

$$CO_3^{--} + H^+ \rightarrow HCO_3^-$$
$$HCO_3^- + H^+ \rightarrow H_2O + CO_2$$
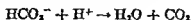
With phenolphthalein in the cold, an end point is obtained when the first stage only has taken place.

With an insoluble alkaline-earth carbonate, on the other hand, the carbonate does not begin to dissolve until the solution is more acid than corresponds to the

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[1] Küster recommends that, in titrating carbonates with methyl orange, a blank experiment be made to see how much effect an equal amount of water saturated with carbon dioxide has upon the same amount of indicator solution. (Z. anorg. Chem., 13, 140.)

[2] Z. anal. Chem., 21, 102 (1892).

[3] Z. anorg. Chem., 13, 140.

phenolphthalein end point, so that a mixture of soluble $Ba(OH)_2$ and insoluble $BaCO_3$ can be titrated with acid and an end point detected as soon as the $Ba(OH)_2$ has been completely neutralized provided that phenolphthalein is the indicator. With methyl orange, on the other hand, a permanent end point will not be reached until all the insoluble carbonate has dissolved.

Procedure. Weigh out into 250-ml Erlenmeyer flasks, two samples of about 1 g each. Record the weights to four significant figures.[1] Fill a glass-stoppered buret with standardized hydrochloric acid and a plain buret with standardized sodium hydroxide. Record the initial readings in the notebook to the nearest 0.01 ml.

Cover the sample with 25 ml of water and add 2 drops of methyl orange indicator solution. Run in acid slowly until the indicator turns distinctly red, rotating the contents of the flask. With an insoluble carbonate, it will be necessary to add a few milliliters of excess acid. When all the carbonate is decomposed, wash down the sides of the flask and carefully add sodium hydroxide from the buret while keeping the liquid in the flask in motion. Stop adding the hydroxide as soon as the liquid becomes distinctly yellow. Finally add acid dropwise until the well-mixed solution shows a faint change toward the pink. In order to determine the end point accurately, the beginner should have two comparison solutions both containing the same amount of indicator as used in the analysis and approximately the same volume as at the end of the titration. For one solution have the indicator in distilled water; the color will be yellow, because water reacts basic to methyl orange. For the other comparison solution, add a drop of the standardized acid, or just enough to change the methyl orange color toward the pink. This shade should be matched in the titration.[2]

From the total volume of hydrochloric acid used, deduct the volume of hydrochloric acid corresponding to the sodium hydroxide added, and this will give the volume of hydrochloric acid actually required to react with the weight of the carbonate used. The milliequivalent weight of Na_2CO_3 in this determination is the molecular weight divided by 2000; the same is true of Na_2O.

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[1] See p. 20, regarding significant figures. In general, no more significant figures should be used in analyses than the accuracy of the result warrants. In reporting results, the next to the last figure kept should not vary by more than two units.

[2] It is also well to have as much neutral sodium chloride present as will be formed by the titration.

3. Determination of Alkali Carbonate and Hydroxide in the Presence of One Another

Method of C. Winkler

Of the many methods which have been proposed for this determination that of Winkler is the best.

In one portion determine the total amount of alkali present by titration with acid, using methyl orange as an indicator, and determine the hydroxide in a second portion as follows: Add the solution from a pipet to enough barium chloride solution to leave the solution about 0.1 N in Ba^{++} after all the carbonate is precipitated; the following reactions take place:

$$Na_2CO_3 + BaCl_2 = 2NaCl + BaCO_3 \text{ (insoluble)}$$
$$2NaOH + BaCl_2 = 2NaCl + Ba(OH)_2 \text{ (soluble)}$$
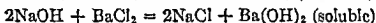
Add phenolphthalein and titrate slowly with hydrochloric acid with constant stirring; decolorization is effected as soon as the hydroxide is neutralized before any barium carbonate is dissolved. The amount of acid used corresponds to the amount of hydroxide originally present.

4. Determination of Alkali Carbonate in the Presence of Either Alkali Hydroxide or Alkali Bicarbonate

If a solution of sodium hydroxide is titrated with tenth-normal hydrochloric acid, the reaction is practically complete at about $pH = 11$. When sodium carbonate, Na_2CO_3, is titrated with tenth-normal hydrochloric acid, it is completely changed to $NaHCO_3$ at about $pH = 10$ and the sodium bicarbonate is changed to chloride at about $pH = 4$. It happens, fortunately, that the color change with phenolphthalein takes place after the sodium hydroxide has been completely neutralized and just after the carbonate has been converted to bicarbonate. Methyl orange, on the other hand, does not show an acid reaction until the sodium bicarbonate is changed completely to sodium chloride.

$$\left.\begin{array}{l} OH^- + H^+ \rightarrow H_2O \\ CO_3^{--} + H^+ \rightarrow HCO_3^- \end{array}\right\} \text{end point with phenolphthalein}$$
$$HCO_3^- + H^+ \rightarrow H_2O + CO_2 \uparrow \text{ additional reaction with methyl orange}$$
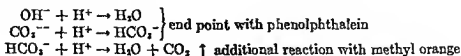
In carrying out the analysis it is important to make sure that there is no loss of CO_2 before the first end point is reached; the solution must be cold, the acid must be added slowly, and each portion must be stirred in well before fresh acid is added.

Procedure. Weigh out 5 g of the sample to four significant figures, dissolve in water, and make up to exactly 500 ml in a measuring flask. Mix well by pouring back and forth into a beaker at least four times,

nnd take 25-ml portions of the solution with a pipet for the further nnalysis.

To one portion, add some phenolphthalein indicator, chill by placing the flask in ice water, and titrate slowly with 0.1 N hydrochloric acid while stirring constantly. Titrate to match the rose color obtained by adding phenolphthalein indicator to a solution of approximately the same concentration of pure sodium bicarbonate. Let T_1 represent the milliliters of acid required to decolorize the solution.

To nnother portion add methyl orange and titrate till the color of the solution begins to change from yellow to pink. Let T_2 represent the total milliliters of acid used to make the solution acid to methyl orange.

Computation. (a) If T_2 is more than twice as large as T_1, the original sample is a mixture of carbonate and bicarbonate. (b) If T_2 is less than twice as large as T_1 the sample contains carbonate and hydroxide.

(a) Now n moles of CO_3^{--} react with n moles of H^+ io the phenolphthalein titration and with $2n$ moles of H^+ in the methyl orange titration; m moles of HCO_3^- react with no acid in the first titration and with m moles of H^+ in the second titration. In a mixture of n moles of CO_3^{--} and m moles of HCO_3^-, when T_1 ml of N-normal HCl is used in the phenolphthalein titration and T_2 ml of acid in the methyl orange titration:

$$T_1 \times N = n = \text{number of millimoles of } CO_3^{--}$$

$$(T_2 - 2T_1)N = m = \text{number of millimoles of } HCO_3^-$$

(b) If T_2 is less than twice as large as T_1, the original sample is a mixture of alkali hydroxide and carbonate:

$$(T_2 - T_1)N = \text{number of millimoles of } CO_3^{--}$$

$$(2T_1 - T_2) \times N = \text{number of millimoles of } OH^-$$

Note. This method of analysis, which applies to the analysis of alkali carbonate, hydroxide, and bicarbonate mixtures but not to mixtures of alkaline-earth carbonate with hydroxide and bicarbonate, is not so satisfactory as Winkler's method which depends upon the titration of one sample with methyl orange as indicator and of another sample with phenolphthalein as indicator after treatment with barium chloride, which precipitates barium carbonate. A solution containing soluble alkali or alkaline-earth hydroxide in the presence of insoluble alkaline-earth carbonate can be titrated with acid and the phenolphthalein end point obtained as soon as the hydroxide has been neutralized completely and before any of the insoluble carbonate dissolves. With methyl orange, however, the end point is not reached until all the alkaline-earth carbonate has dissolved. The carbonate dissolves very slowly toward the last, it is best, therefore, to add an excess of acid and, then, when all the alkaline-earth carbonate is dissolved, titrate back to a methyl orange end point.

5. Determination of Alkaline-Earth Hydroxides

Titrate with phenolphthalein as indicator to a colorless end point.

6. Determination of Alkaline-Earth Carbonates

Cover the carbonate with 25 ml of water, add an excess of the standard acid, boil to remove the carbon dioxide, cool, and titrate the excess of acid with alkali and in the methyl orange as indicator

7. Determination of Alkaline-Earth Oxide together with Alkaline-Earth Carbonate

This analysis is based upon the fact that calcium carbonate, as well as calcium oxide, neutralizes a solution which is acid to methyl orange and changes the color of the indicator. One mole of $CaCO_3$ reacts with 2 moles HCl before the solution is acid to methyl orange. Toward phenolphthalein, calcium oxide is basic but calcium carbonate is not, and the end point is reached when all the calcium oxide is neutralized and the calcium carbonate begins to dissolve.

Suppose, for example, that it is desired to determine the amount of oxide and carbonate in a sample of "quicklime." Break up the lime into pieces about the size of a pea, weigh out 14 g, and slake with boiled water. Wash the paste into a 500-ml flask and dilute to the mark with water free from carbon dioxide. After thoroughly mixing, transfer 50 ml of the turbid liquid to a second 500-ml flask and again dilute to the mark.

Determination of the Total Calcium. To 50 ml (0.14 g of substance) of the last solution add 60 ml of 0.1 N hydrochloric acid and heat until there is no further evolution of carbon dioxide. Cool, and titrate the excess of acid with 0.1 N sodium hydroxide solution, using methyl orange as an indicator. For this purpose t ml of methyl orange is required; consequently $60 - t$ ml of 0.1 N acid was necessary to neutralize the calcium hydroxide and calcium carbonate in the 50 ml of the solution taken for analysis.

Determination of the Calcium Oxide. Titrate a second portion of the freshly shaken solution with 0.1 N hydrochloric acid added drop by drop to the cold solution, with phenolphthalein as an indicator. Assume that t_1 ml of the acid was necessary to neutralize the calcium oxide.

Consequently, for the neutralization of the $CaCO_3 + CaO$, $60 - t$ ml of 0.1 N acid was required, and for the CaO, t_1 ml of 0.1 N acid was necessary. For the neutralization of the $CaCO_3$, therefore, $60 - (t + t_1)$ ml of 0.1 N acid was necessary.

50 ml solution (0.14 g lime) contains:

(a) $t_i \times 0.002803$ g CaO, (b) $[60 - (t + t_i)] \times 0.5003$ g CaCO₃, and the sample contains

$$\frac{t_i \times 0.2805}{0.14} = 2t_i \text{ per cent CaO}$$

and

$$\frac{[60 - (t + t_i)] \times 0.5005}{0.14} = \text{per cent CaCO}_3$$

The above method of titration *fails to take into consideration* the fact that commercial lime contains more or less magnesia. As a result of cooperative analyses made by the U. S. Geological Survey, the Bureau of Chemistry, and the Bureau of Standards, using seven methods of analysis, Miss Alice I. Whitson published the following modified Scaife method for the

8. Determination of Available Lime in Quicklime and Hydrated Lime

Weigh 1.402 g of the carefully prepared and finely ground lime (passing 100 mesh) into a 400-ml beaker, add 200 ml of hot water, cover, heat carefully, and then boil for 3 minutes.

Cool, wash down the cover glass, add 2 drops of phenolphthalein and titrate with N hydrochloric acid, adding the acid dropwise as rapidly as possible and stirring vigorously to avoid local excess of acid. When the pink color disappears in streaks, retard the rate of addition of acid somewhat, but continue until the pink color fades throughout the solution for 1-2 seconds. Note the reading and ignore the return of color.

Repeat the experiment, substituting for the 400-ml beaker a 1-l graduated flask carrying a one-hole stopper fitted with a short glass tube drawn out to a point. Cool, and add dropwise, with vigorous stirring, about 4.5 ml less acid than before. Call this number of milliliters used A. Grind up any small lumps with a glass rod flattened at one end, dilute to the mark with freshly boiled distilled water, close the flask with a solid stopper, mix thoroughly for 4-5 minutes, and let settle for half an hour.

Pipet off a 200-ml portion, add phenolphthalein, and *titrate slowly* with 0.5 N hydrochloric acid until the solution remains colorless on standing 1 minute. Call this additional number of milliliters B. Then the percentage of available CaO = $2A + 5B$.

The computation is thus simplified because the weight of sample taken is exactly 50 times the milliequivalent weight of calcium oxide (0.02804 g). If any other weight of sample, s, is taken and hydrochloric acid solutions of N_1 and N_2 concentrations are used instead of

exactly normal and half-normal acids, the computation is as follows:

$$\frac{(A \times N_1 + 5B \times N_2) \times 0.02804 \times 100}{s} = \text{per cent CaO}$$

9. Determination of Alkaline-Earth Bicarbonates

This determination finds a practical application in the determination of the temporary hardness of water.

The hardness of a water is caused by the presence of alkaline-earth salts, either those with strong acids ($CaSO_4$, $MgCl_2$) or bicarbonates. A hard water is recognized by the fact that it gives with a clear soap solution a turbidity or even a precipitate, and considerable soap must be added before a lather is obtained on shaking. Usually calcium salts, and chiefly calcium bicarbonate, predominate in such a solution, and hardness is usually expressed in parts of calcium carbonate (or calcium oxide) in 100,000 parts of water.

If the solution contains 1 part of calcium carbonate in 100,000 parts of water it is said to possess 1 degree of hardness (French); if such a water contains n parts of $CaCO_3$ in the same quantity of water it possesses n degrees of hardness. In Germany the hardness is expressed in parts of CaO per 100,000 parts of water; in England the hardness is expressed in grains of calcium carbonate per Imperial gallon. In the United States hardness is usually expressed in grains of calcium carbonate per U. S. gallon, which is five-sixths as large as the Imperial gallon. One degree of hardness on the French scale = 0.56 degree on the German scale = 0.70 degree on the English scale = 0.585 degree on the U. S. scale. When magnesium salts are present, these are expressed in terms of the equivalent amounts of $CaCO_3$ or CaO. The error caused by this assumption is not great, for the amount of magnesium present is usually small compared with the amount of calcium. If a water containing calcium bicarbonate and calcium sulfate is heated to boiling, the former is decomposed with the precipitation of calcium carbonate:

$$Ca(HCO_3)_2 = H_2O + CO_2 + CaCO_3$$

while the calcium sulfate remains in solution. In other words, the hardness produced by the presence of alkaline-earth bicarbonates disappears on boiling, and is designated, therefore, as "temporary hardness" to distinguish it from "permanent hardness," which is usually caused by alkaline-earth salts of the stronger acids, usually calcium sulfate. The sum of the temporary and permanent hardness of a water represents the total hardness.

According to O. Hehner, the temporary as well as permanent hardness may be determined accurately by an alkalimetric process.

(a) Determination of Temporary Hardness

Place 100 ml of the water to be examined in a white porcelain evaporating dish, add a few drops of methyl orange, and titrate the solution with 0.1 N hydrochloric acid until the first change from yellow to orange takes place. From the amount of hydrochloric acid used the amount of calcium carbonate present can be calculated.

Example:

100 ml water required 2 5 ml of 0 1 N hydrochloric acid

As 1000 ml of 0 1 N hydrochloric acid neutralizes, $\dfrac{CaCO_3}{20} = 5\,003$ g $CaCO_3$, 1 ml of 0.1 N hydrochloric acid will neutralize 0 005005 g $CaCO_3$ and 2.5 ml of 0.1 N hydrochloric acid corresponds to 0 005003 $\times$ 2 5 = 0.0125 g $CaCO_3$.

Then if 100 ml of water contains 0 0125 g $CaCO_3$, 100,000 ml of water will contain 12.5 g $CaCO_3$. This corresponds to 12.5 French degrees or 7.01 U. S. degrees.

(b) Determination of Permanent Hardness

Treat another portion of 100 ml of the water with an excess of 0.1 N sodium carbonate solution, evaporate on the water bath to dryness, and take up in a little freshly boiled distilled water. Filter off the residue and wash 4 times with hot water. Allow the filtrate to cool and afterwards titrate with 0.1 N hydrochloric acid, using methyl orange as indicator. If the amount of hydrochloric acid used for the titration is deducted from the total amount of sodium carbonate added to the water, the difference represents the amount of sodium carbonate required for the precipitation of the alkaline-earth salts of the strong acids.

Example. 100 ml of water + 10 ml of 0.1 N Na_2CO_3 were evaporated to dryness, the residue extracted with water, and the filtrate titrated with 0.1 N hydrochloric acid; this required 8 7 ml of HCl. Consequently, for the precipitation of the calcium sulfate 10 − 8.7 = 1.3 ml of 0.1 N Na_2CO_3 was necessary, which corresponds to 1.3 $\times$ 0 005 = 0.0065 g $CaCO_3$ per 100 ml water and 6 5 g $CaCO_3$ per 100,000 ml of water.

The permanent hardness amounts to 3.8 U. S degrees.

Remark. The above methods of Hehner for the determination of hardness will give reliable results only when the water contains no alkali carbonates in solution, as is usually the case with drinking waters For the determination of the amount of alkaline earth present in many *mineral waters* it is obvious that these methods cannot be used

10. Determination of Alkaline-Earth Salts of Strong Acids

The determination is practically the same as was indicated above. The alkaline-earth salt is precipitated by means of an excess of titrated sodium carbonate solution, and after filtration this excess is determined by titrating back with acid.

Procedure. A solution containing calcium chloride and hydrochloric acid is to be analyzed. Place it in a measuring flask, treat w'th a few drops of methyl orange and with sodium hydroxide solution until the neutral point is reached; after this add an accurately measured amount of sodium carbonate solution. Heat the solution until the precipitated calcium carbonate becomes crystalline, allow to cool, dilute to the mark, mix, filter through a dry filter, and titrate the excess of sodium carbonate titrated in an aliquot part of the filtrate. From the amount of sodium carbonate required for the precipitation of the calcium the amount of the metal can be calculated.

Remark. Other metals which are precipitated by sodium carbonate can be determined in this way.

11. Titration of Borates and Phosphates

Boric acid, H_3BO_3, is such a weak acid that it cannot be titrated accurately with $0.1\ N$ alkali hydroxide. Its ionization constant is 5×10^{-10}. It behaves as a monobasic acid, and the salts are derived from metaboric acid, HBO_2, or pyroboric acid, $H_2B_4O_7$, both of which are also very weak acids. Borax, $Na_2B_4O_7$, the best-known salt of pyroboric (or tetraboric) acid, can be titrated with acid with methyl orange or methyl red as indicator according to the reaction:

$$B_4O_7^{--} + 2H^+ + 5H_2O \rightarrow 4H_3BO_3$$
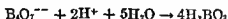
Commercial samples of borax often contain some alkali carbonate or bicarbonate together with a small quantity of other borates. If the aqueous solution of borax is neutralized to methyl orange and then an organic compound containing more than one hydroxyl group is added such as glycerol, $C_3H_5(OH)_3$, mannitol, $C_6H_8(OH)_6$, dextrose, $C_6H_{12}O_6$, or invert sugar (a mixture of dextrose and its isomer levulose) a stronger complex acid is formed which can be titrated with alkali hydroxide in the presence of phenolphthalein. Mannitol is very effective in this respect, and 0.5–0 7 g of it is sufficient for about 10 milliequivalents of boric acid.

If, therefore, a solution of pure $Na_2B_4O_7$ is titrated with HCl to a methyl orange or methyl red end point, two molecules of HCl will be required for each molecule of borax. If then the neutralized solution is treated with mannitol, glycerol, or invert sugar, four molecules of NaOH will be required to make the solution neutral to phenolphthalein. If, on the other hand, a fresh sample of the borax is dissolved and treated with mannitol, glycerol, or invert sugar, two molecules of NaOH will be required to make the solution neutral to phenolphthalein. In other words, the equivalent weight of borax is $Na_2B_4O_7 \div 2$ when it reacts with HCl to a methyl orange end point, and the equivalent weight is the same when the acid is strengthened by adding one of the above-mentioned hydroxy organic compounds and the titration is then made with alkali hydroxide.

this book estimate the approximate amount of acid present. Dilute a weighed amount of the acid so that the solution will have approximately the same concentration as that of the alkali hydroxide to be used for the titration. The weighing can take place in a glass-stoppered weighing tube. Analyze by one of the following methods:

1. Place an accurately measured portion of the diluted acid (20–25 ml) in a beaker, add methyl orange, and titrate the solution with sodium hydroxide solution until a yellow color is obtained.

2. Place the diluted solution to be analyzed in a buret, and titrate with it a definite volume of normal alkali hydroxide solution.

3. Titrate a definite volume of the diluted acid with 0.1 N Ba(OH)$_2$ solution or with sodium hydroxide free from carbonate, using phenolphthalein as an indicator.[1]

Example. For the analysis 0.5 N NaOH was used.

The hydrochloric acid analyzed had at 15° a density of 1.122, corresponding to about 24 per cent HCl by weight.

One hundred milliliters 0.5 N sodium hydroxide is equivalent to 1.823 g of HCl, and consequently $\dfrac{1.823}{0.24}$ = 7.595 g of the above acid would be required to make 100 ml of 0.5 N acid, if it contained exactly 24 per cent HCl. Weigh out about this quantity (say 8 g), and as the density of the solution is 1.122, this will require $\dfrac{8}{1.122}$ ≈ 7 ml. Place 7 ml of the acid in a tared, glass-stoppered weighing tube, weigh the tube and its contents, rinse the latter into a 100-ml measuring flask, and dilute with distilled water up to the mark. After thoroughly mixing, measure off 25 ml of the acid and analyze by one of the above methods. If in an analysis the original weight of the acid amounted to 7.962 g and 25 ml of the diluted acid required 25.80 ml of 0.5 N alkali, then 100 ml would require 25.80 × 4 = 103.2 ml of 0.5 N alkali, corresponding to 103.2 × 0.01823 = 1.881 g HCl. The acid, therefore, contains $\dfrac{1.881 \times 100}{7.962}$ = 23.6 per cent HCl.

Remark. Instead of weighing out the acid for the analysis, it can be measured and from the percentage by volume found the percentage by weight calculated. However, as the density as determined by an aerometer is not very accurate, it is better to weigh the acid. If the density of the acid is taken with a pycnometer, using all necessary precautions (cf. Kohlrausch, *Leitfaden der praktischen Physik*), it is a matter of indifference whether the acid used for the analysis is weighed or measured.

2. Determination of Total Acid in Vinegar

Weigh a glass-stoppered weighing tube to the nearest milligram. Add to it about 5 ml of vinegar, and reweigh. Transfer to a 200-ml

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[1] When phenolphthalein is used as an indicator in cold solutions the acids must be diluted with water free from carbonate.

Erlenmeyer flask, and dilute with cooled, boiled water until the color of the solution is not enough to interfere with a phenolphthalein end point. Add phenolphthalein indicator, and titrate with 0.5 N NaOH which is free from carbonate (see p. 485). Analyze three separate portions; the average deviation should not exceed 2 parts per 1000. Report the percentage of acetic acid (equivalent weight 60.05), and assume that this is the only acid present.

3. Determination of the Acid Content of Fuming Acids

Determination of the Acid Content of Oleum (Fuming Sulfuric Acid)

Highly concentrated acids must be always weighed and not measured volumetrically, in order to avoid loss by evaporation. The weighing is best accomplished by means of the Lunge-Rey pipet, shown in Fig. 83, but a glass-stoppered weighing tube can be used as in the analysis of vinegar.

Remove the lower tube, introduce 0.5 ml of water, and weigh together with the dry upper pipet, but leaving the two parts unconnected. Close the lower stopcock, open the upper one, and produce a slight vacuum in the bulb by sucking through the upper tube and then closing the stopcock. Dip the dry point of the pipet into the fuming acid (if it is of solid pyrosulfuric acid, first melt it by warming slightly), and open the lower stopcock. As soon as the widened part of the pipet below the lower bulb is one-half to three-fourths full, close the stopcock, taking care that none of the liquid reaches up to it.

Carefully wipe off the acid on the outside of the pipet with filter paper; connect the two parts of the pipet and again weigh. The quantity of acid taken for the analysis should amount to 0.5–1 g. Dip the point of the pipet into about 100 ml of distilled water contained in a beaker, and, by opening first the upper stopcock and then the lower, allow the acid to run into the water. Rinse out the pipet, add the rinsings to the contents of beaker, add methyl orange, and titrate with 0.5 N sodium hydroxide.
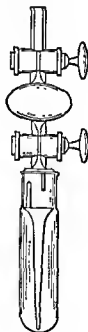
Fig. 83.

Computation. Fuming sulfuric acid can be considered to be a solution of anhydrous SO_3 in H_2SO_4 [1]. On treatment with water, the following reaction takes place:

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[1] Fuming sulfuric acid contains a little SO_2 but as its determination involves an iodimetric titration it will not be considered here. The analysis of fuming sulfuric acid is not a suitable exercise for beginners, but the method is described because the calculation should be understood.

$SO_3 + H_2O = H_2SO_4$. The titration with NaOH, therefore, shows the total acid present, including that formed from the anhydride. Let p be the weight of the original sample and n the milliliter of N-normal NaOH used. The total weight of H_2SO_4 (equivalent weight 49) in the solution after the reaction with water is

$$n \times N \times 0.049 = p_2$$

Then $p_2 - p$ is the weight of the water which reacted with the anhydrous SO_3. Since 1 mole of H_2O (18.02 g) reacts with 1 mole of SO_3 (80.06 g), evidently 1 g of H_2O reacts with $80.06 \div 18.02 = 4.443$ g of SO_3 and $p_2 - p$ grams of water are equivalent to $4.443 (p_2 - p)$ grams of anhydrous SO_3. This value subtracted from the weight, p, gives the original weight of H_2SO_4.[1]

Fuming hydrochloric acid can be analyzed in the same way as fuming sulfuric acid, and the computation is simple. In the case of fuming nitric acid, it is best to add an excess of alkali hydroxide before adding the methyl orange and then titrate back with 0.5 N hydrochloric acid; in this way the decolorization of the indicator by the ever-present nitrous acid is avoided.

4. Titration of Hydroxylamine Salts

Hydroxylamine hydrochloride reacts neutral towards methyl orange and acid towards phenolphthalein. If phenolphthalein is added to an aqueous solution of the salt, and the titration is made with 0.1 N alkali, the end point will be obtained when the total amount of acid present has been neutralized by the alkali. It is impossible to determine the amount of free hydrochloric acid present when phenolphthalein is used, but it can be done with methyl orange. Romijn[2] recommends for the titration of the acid a 0.1 N borax solution.

5. Hydrofluoric Acid

1000 ml normal alkali = HF = 20.01 g HF

Hydrofluoric acid can be titrated with phenolphthalein as an indicator, but not with methyl orange. Measure out the acid into a

---

[1] This value 80.06 ÷ 18.02, or SO_3/H_2O, where each formula represents a molecular weight, is what is called a *chemical factor*. It represents the weight of SO_3 corresponding to a unit weight of H_2O so that, if the weight of water is known, the corresponding weight of SO_3 is obtained by multiplying the weight of water by this chemical factor. The chemical factor represents the weight ratio of weight desired ÷ weight obtained, but it is necessary always to use equivalent quantities in such chemical factors. Thus if 1 molecule of H_2O reacted with 2 molecules of SO_3, the chemical factor would be $2SO_3/H_2O$.

[2] *Z. anal. Chem.*, **36**, 19 (1897). This method has not been tested in the author's laboratory.

platinum dish by means of a pipet which is coated with beeswax, add an excess of sodium hydroxide free from carbonate, and titrate the excess of the latter in hot solution with an acid of known strength.[1]

A neutral fluoride can be titrated with fair accuracy by adding neutral ferric chloride solution until an end point is obtained with KCNS as indicator.[2]

$$6NaF + FeCl_3 = Na_3FeF_6 + 3NaCl$$
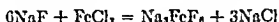
Considerable sodium chloride should be added to precipitate the complex salt.

6. Fluosilicic Acid

The titration of this acid can take place according to either of the following reactions:

I. $H_2SiF_6 + 2KOH = K_2SiF_6 + 2H_2O$

II. $SiF_6^{--} + 6OH^- = 6F^- + 2H_2O + Si(OH)_4$

According to Equation I

1000 ml normal KOH or Ba(OH)$_2$ = 72.04 g H$_2$SiF$_6$
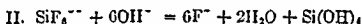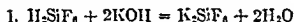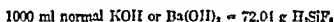
Treadwell's Method

If fluosilicic acid is titrated in the cold with potassium hydroxide in the presence of phenolphthalein as indicator, a red color appears after a time but disappears later on account of the excess alkali hydroxide reacting with K$_2$SiF$_6$ to form 6KF and Si(OH)$_4$.

This last reaction, however, takes place so slowly that it is impossible to obtain a distinct end point. If the solution is diluted with an equal volume of alcohol, however, then 2 or 3 drops of phenolphthalein added, the secondary reaction is prevented and the acid can be titrated with tenth-normal potassium or barium hydroxide. The insoluble potassium or barium fluosilicate separates out and is not acted upon by an excess of the alkali, so that a sharp end point is obtained as soon as all the H$_2$SiF$_6$ has been changed to K$_2$SiF$_6$. Sodium hydroxide forms a soluble salt so that the titration cannot be made with this reagent.

Indirect Method of Penfield[3]

Penfield treated the solution to be titrated with an excess of KCl, diluted with an equal volume of alcohol, and then titrated the hydro-

[1] Cf. Winteler, Z. anger. Chem., 1902, 33.
[2] Greeff, Ber., 36, 2511 (1913).
[3] Chem. News, 32, 179.

chloric acid set free in the reaction

$$H_2SiF_6 + 2KCl = K_2SiF_6 + 2HCl$$
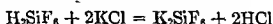
with tenth-normal sodium hydroxide solution and with cochineal as indicator. Methyl red is preferable to the cochineal.

Remark. The precipitate of K_2SiF_6 produced by the treatment with KCl and alcohol can be titrated, as in the following method, with 4 molecules of alkali hydroxide.[1]

$$K_2SiF_6 + 4OH^- \rightarrow H_4SiO_4 + 2K^+ + 6F^-$$

According to Equation II

1000 ml normal NaOH = 24 01 g H_2SiF_6
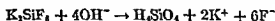
(a) Method of Sahlbom and Hinrichsen[2]

Titrate the solution at the temperature of the water bath with tenthnormal sodium hydroxide solution, using phenolphthalein as indicator.

(b) Method of Schucht and Möller[3]

Treat the solution to be titrated with an excess of neutral calcium chloride solution (25 ml of $4\,N$ $CaCl_2$) and titrate with tenth-normal sodium hydroxide, using methyl orange as indicator. The following reaction takes place in the cold:

$$H_2SiF_6 + 3CaCl_2 + 6NaOH = 3CaF_2 + 6NaCl + Si(OH)_4 + 2H_2O$$

During the titration the solution remains clear, for the CaF_2 and the $Si(OH)_4$ remain in colloidal solution. Phenolphthalein should not be used as indicator, as it is hard to decide upon the correct end point.

In the titration of salts of fluosilicic acid, however, the titration must always be carried out with phenolphthalein as indicator:

$$Na_2SiF_6 + 3CaCl_2 + 4NaOH = 3CaF_2 + 6NaCl + Si(OH)_4$$

In this case

1000 ml of normal NaOH = 47.01 g of Na_2SiF_6
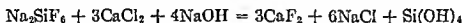
7. Determination of Organic Acids

Methyl orange cannot be used for the titration of organic acids, but phenolphthalein is suitable in most cases. If the ionization constant of the acid is known the approximate pH at the end point can be calcu-

[1] Cf. Hilemann, Z. anorg. Chem., 51, 159 (1906); Travers, C. A., 16, 540 (1922).
[2] Ber., 39, 2609 (1906).
[3] Ber., 39, 3693 (1906).

lated (cf. p. 476) and the appropriate indicator chosen (p. 463). If carbonic acid is present at the same time, the titration can be made in a hot solution (cf. p. 489). It is best to dilute the organic acid with water free from carbon dioxide, add phenolphthalein, and titrate with half-normal barium hydroxide in the cold.

To illustrate. It is desired to analyze a sample of acetic anhydride. The only impurity that the distilled product is likely to contain is acetic acid, so that it is a question of determining the amount of acid and anhydride in the presence of one another. Such a problem can be solved only by an indirect analysis. Weigh out the mixture in a small glass bulb and drop it into an accurately measured volume of standard barium hydroxide solution contained in a flask which is connected with a return-flow condenser and a soda-lime tube at the top. Heat gently until the anhydride has dissolved completely; it is thereby changed to acetate and the total quantity of acetate formed corresponds to the neutralization of the acetic acid originally present together with that formed by the hydrolysis of the anhydride by the reaction

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3CO \cdot OH$$
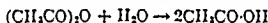
After the reaction is complete, add phenolphthalein indicator solution and titrate the excess $Ba(OH)_2$ with $0.1\ N$ HCl.

Calculation: *First Method.* Subtract, from the total milliequivalents of base added, the milliequivalents of acid used; this gives the milliequivalents of $Ba(OH)_2$ neutralized by the acetic acid including that originally present and that formed as a result of the hydrolysis of the anhydride. This number multiplied by 0.0605 (the equivalent weight of CH_3CO OH) gives the total weight of acetic acid neutralized. Call this weight q. Then if x is the weight of acetic anhydride originally present, $p - x$ is the weight of the acetic acid present in p g of the sample, and

$$\frac{2CH_3CO\ OH}{(CH_3CO)_2O}\ x + p - x = q$$

Second Method. The weight q is larger than the weight p because one molecule of water has combined with each molecule of acetic anhydride. The weight of anhydride, therefore, is

$$\frac{(CH_3CO)_2O}{H_2O}\ (q - p)$$

Then if x g of anhydride and y g of acetic acid are present in p g of sample, we have

$$x + y = p$$

$$m x + y = q \text{ (acetic acid)}$$

from which can be computed

$$x = \frac{q - p}{m - 1}$$

In this equation

$$m = \frac{2C_2H_4O_2}{C_4H_6O_3} = \frac{120.10}{102.05} = 1.177$$

and

$$\frac{1}{m - 1} = 5.65$$

Remarks. 1. An indirect analysis such as this is not very accurate because the equivalent weight of acetic acid is 60.05 and that of acetic anhydride is 51.05. Absolutely pure acetic anhydride yields only 1.18 times its weight of acetic acid. Any error in determining the acetic acid content after hydrolysis is multiplied by about 5.5 in determining the percentage composition of the mixture.

2. Acetic acid anhydride is also hydrolyzed by water at the ordinary temperature. If a weighed amount of the substance is shaken with water in a flask until no more drops of anhydride are to be recognized and the acetic acid formed is then titrated with barium hydroxide, using phenolphthalein as indicator, correct results are obtained if the water used is entirely free from carbon dioxide. It is always safer, however, to carry out the determination as outlined above.

8. Determination of Sulfurous Acid

For the determination of sulfurous acid by itself, the analysis is best accomplished, as recommended by Volhard, by an iodimetric process, i.e., it is oxidized to sulfuric acid. In many cases, however, it is necessary to titrate the sulfurous acid with alkali hydroxide (cf. p. 469). Methyl orange should be used as indicator, and only one hydrogen in the H_2SO_3 is titrated.

Titration with phenolphthalein gives approximately complete neutralization, but the results are reliable only when an excess of neutral hydrogen peroxide is added, which oxidizes the sulfurous acid.

9. Determination of Thiosulfuric Acid[1]

To a large excess of mercuric chloride (20 ml of the cold, saturated solution for each millimole of $Na_2S_2O_3$) add a measured volume of sodium thiosulfate solution. Shake several times and allow to stand 5 minutes. Then to prevent precipitation of HgO, add 30 ml of $4 N$ ammonium chloride solution, and titrate with $0.1 N$ sodium hydroxide

[1] W. Feld, Z. angew. Chem., 24, 290, 1161 (1911); A. Sander, ibid., 1915, 9; 1916, 16.

and methyl orange as indicator:

$$(a) \quad 2Na_2S_2O_3 + 2HgCl_2 = 2HgS_2O_3 + 4NaCl$$
$$(b) \quad 2HgS_2O_3 + 2H_2O = 2HgS + 2H_2SO_4$$
$$(c) \quad 2HgS + HgCl_2 = Hg_3S_2Cl_2$$
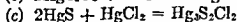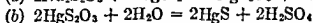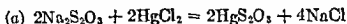
If too little $HgCl_2$ is present, black mercuric sulfide precipitates and makes the titration difficult.

Polythionates can be titrated similarly,[1] as the following equations show:

$$2K_2S_3O_6 + 3HgCl_2 + 4H_2O = Hg_3S_2Cl_2 + 4KCl + 4H_2SO_4$$
$$2K_2S_4O_6 + 3HgCl_2 + 4H_2O = Hg_3S_2Cl_2 + 2S + 4KCl + 4H_2SO_4$$
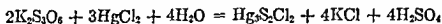
According to Eliasberg,[2] the thiosulfates and polythionates can be determined by treatment with a measured quantity of alkali hydroxide solution and neutral hydrogen peroxide, boiling to complete the oxidation, and titrating the excess of base with 0.1 N acid.

$$Na_2S_2O_3 + 4H_2O_2 + H_2O = Na_2SO_4 + 4H_2O + H_2SO_4$$
$$Na_2S_4O_6 + 7H_2O_2 + 2H_2O = Na_2SO_4 + 6H_2O + 3H_2SO_4$$
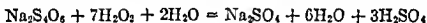
10. Determination of Orthophosphoric Acid

NaH_2PO_4 reacts acid toward phenolphthalein and neutral toward methyl orange; Na_2HPO_4 is neutral toward the former indicator and basic toward the latter. Therefore, on titrating free phosphoric acid with alkali one of the following reactions will take place:

1. $H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O$ (phenolphthalein).

2. $H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$ (methyl orange).
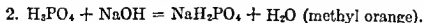
The first reaction is not altogether sharp, because pure Na_2HPO_4 is hydrolyzed slightly, so that it becomes alkaline to phenolphthalein:

$$Na_2HPO_4 + HOH \rightleftarrows NaH_2PO_4 + NaOH$$
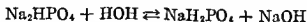
To prevent this hydrolysis, the titration is best effected in a small volume of cold half-saturated sodium chloride solution (cf. p. 505).

[1] Kessler, *J. prakt Chem*, **47**, 42 (1849).
[2] *Ber.*, **19**, 322 (1866).

11. Alkalimetric Determination of Phosphorus in Iron and Steel

1000 ml normal NaOH ≈ 1.349 g P

Procedure for Carbon Steels and Alloy Steels Soluble in Nitric Acid. Use of Acid Ammonium Molybdate Reagent

Plain Carbon Steel. Weigh 2 g of steel to the nearest centigram into a 300-ml Erlenmeyer flask; to this add 100 ml of approximately 4 N nitric acid, and insert a small, short-stemmed funnel into the neck of the flask. Heat until the sample is entirely dissolved and very little oxide of nitrogen is visible in the neck of the flask. Add 10 ml of 1.5 per cent $KMnO_4$ solution and boil gently for 2 to 3 minutes. The purpose of the permanganate is to oxidize the dissolved carbide and to make sure that all the phosphorus is fully oxidized to phosphoric acid. If no precipitate appears, add more permanganate and boil again. Dissolve the precipitate of MnO_2, and reduce the excess $KMnO_4$ by adding a few drops of sulfurous acid, a small crystal of ferrous sulfate, or some 5 per cent sodium thiosulfate solution. Add very little of the reducing agent at a time, but continue adding it, at short intervals, until the manganese dioxide is dissolved. If there is any appreciable silicious residue at this point it should be removed by filtration. Boil 2 minutes after the manganese dioxide has dissolved, and then cool to 40°. If the volume of the solution is less than about 80 ml at this stage of the analysis, more 4 N nitric acid should be added. Add 40 ml of 6 N ammonium hydroxide in portions of 25, 10, and 5 ml, and rotate the flask until the precipitated ferric hydroxide redissolves. It is important that the solution should now assume a pale straw color and not appear at all red from colloidal ferric hydroxide. A red solution shows that too much ammonia was added and more nitric acid must be added or the precipitation of the phosphorus will be incomplete. With the solution at about 40° add 40 ml of the acid ammonium molybdate solution (see p. 373). Stopper the flask with a rubber stopper and shake vigorously for 5 minutes; allow the precipitate to settle for 15 minutes but in no case for more than half an hour.

Filter off the precipitate and use a 9-cm ashless filter paper that fits the funnel tightly. Wash the flask, precipitate, and paper twice with 5-ml portions of 1 per cent HNO_3 (1 ml concentrated acid to 100 ml of water) and then 5 times with 5-ml portions of 1 per cent KNO_3 solution. Finally wash the paper with cold 1 per cent KNO_3 until 10 ml of the last filtrate will not decolorize 1 drop (0.03 ml) of 0.1 N NaOH and 1 drop of phenolphthalein indicator solution. This usually requires about 10 washings more than are specified above. Direct the dilute KNO_3

solution around the edge of the filter and then spirally down, and wait until the liquid has drained before washing again.

Return the paper and the precipitate to the Erlenmeyer flask in which the precipitation took place, add 25 ml of water, 2 drops of phenol-phthalein indicator solution, and, from a buret or pipet, 10 ml of 0.1 N NaOH free from carbonate. This will usually be sufficient to dissolve all the yellow precipitate and leave the solution alkaline to phenol-phthalein. If necessary add more NaOH. Discharge the pink color by adding a measured volume of 0.1 N HNO_3 from a buret, and finish the titration by adding just enough more of the 0.1 N NaOH to impart a pink color to the solution.

The chemical equation that represents the dissolving of the precipitate, with the solution left neutral to phenolphthalein (cf. p. 471), is the following

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 23OH^- \rightarrow 12MoO_4^{--} + 3NH_4^+ + HPO_4^{--} + 11H_2O$$

From this equation it is clear that

$$1P \approx 12Mo \approx 23OH^-$$

and the milliequivalent weight of phosphorus by this method of analysis is P/23,000 ≈ 0 001349 g of phosphorus.

Alternative Procedure. Use of Ammoniacal Ammonium Molybdate Reagent[1]

Treat 2 g of steel in a 300-ml Erlenmeyer flask with 50 ml of 6 N HNO_3. When the sample has dissolved add a slight excess of 2.5 per cent $KMnO_4$ solution (3-10 ml) to complete the oxidation. An excess is shown by the formation of MnO_2 precipitate or a persistent perman-ganate color. Dissolve the precipitate and reduce the excess perman-ganate by adding a few drops of sulfurous acid, sodium sulfite, or alkali nitrite, and boil to expel oxides of nitrogen and sulfur. Cool to about 70° and add 50 ml of ammonium molybdate prepared according to Johnson or to the A.S.T.M. formula (see p. 373). Stopper the flask, shake vigorously for 10 minutes, preferably mechanically, cool to 20° or below, and filter. Treat the precipitate as in the previous procedure.

Modifications for Other Iron Alloys

Cast Iron. Dissolve 0 5-1 g of sample in half the quantity of HNO_3 recommended above, but after the oxidation with $KMnO_4$ filter through paper.

Nickel, Chrome-Nickel, Stainless, and Similar Alloy Steels Containing neither Tungsten nor Vanadium. If the sample does not dissolve in dilute nitric acid, treat

[1] *Sampling and Analysis of Carbon and Alloy Steels* Methods of the Chemists of the United States Steel Corporation as Revised to 1937.

2 g of steel with 50 ml of a mixture of equal parts concentrated nitric and concentrated bydrochloric acids, and to the solution add 20 ml of concentrated $HClO_4$ (48 per cent $HClO_4 = 27 N$). Evaporate to fumes of $HClO_4$ and continue beating 5 minutes to oxidize Cr to chromic acid and to dehydrate any silica. Cool somewhat, add 40 ml of water, filter, and wash with cold water.

Add dropwise a saturated solution of SO_2 until all the chromium and vanadium are reduced, and boil until the excess SO_2 is expelled. With the filtrate at about 90°, add 50 ml of either of the slightly ammoniacal ammonium molybdate reagents (p. 373) and shake well for 5 minutes. Filter and wash in the usual manner.

High-Speed Steels or Other Steels Containing Tungsten and Vanadium. Treat 3 g of steel with 60 ml of 4 N HNO_3. Add 30 ml of concentrated HCl and evaporate to dryness. Take up the residue in 20 ml of 6 N HCl with gentle beating. Dilute to 100 ml with hot water and filter off the WO_3. Evaporate the filtrate twice with 20-ml portions of concentrated HNO_3 to expel the HCl, but be careful not to bake the residue. Carry the second evaporation to the point where the residue is sirupy, add 100 ml of 4 N HNO_3, and filter. Wash the residue with cold water, and neutralize with 40 ml of 6 N NH_4OH. Cool the solution to 15°; add 5 ml of approximately 1.5 N ferrous sulfate solution (400 g $FeSO_4 \cdot 7H_2O$ per liter) to reduce the vanadic acid and 2–3 drops of saturated sulfurous acid. Add 75 ml of the *acid* ammonium molybdate reagent, shake for 10 minutes, and allow to stand 4 hours or more before filtering off the yellow ammonium phosphomolybdate precipitate.

In the above directions and throughout the book concentrated nitric acid refers to the 16 N acid of density 1.42 and concentrated bydrochloric acid to the 12 N acid of density 1.2.

12. Determination of Boric Acid

Free boric acid has no action upon methyl orange, consequently alkali borates may be titrated with hydrochloric and nitric acids, using this indicator; with sulfuric acid the results are not so satisfactory, for there is then no sharp color change. If phenolphthalein is used as the indicator, the red color fades gradually and the end point cannot be determined with certainty. If, on the other hand, sodium hydroxide is slowly run into an aqueous solution of boric acid containing phenolphthalein, after some time a pale pink color is noticeable which becomes deeper on the addition of more alkali. The first pink color is formed before all the boric acid has been neutralized, for sodium borate is perceptibly hydrolyzed. Free boric acid cannot be titrated by itself, but if, as proposed by Jörgensen,[1] a sufficient amount of glycerol[2] (or mannitol[3]) is added to the solution, the hydrolysis is prevented, so that when 1 mole of NaOH is present for 1 mole of H_3BO_3 the solution suddenly changes from colorless to red; probably a stronger acid is formed by the addition of the glycerol, the glyceryl-boric acid $(C_3H_5O_2OH)B(OH)$.

[1] *Z. Nahrungsm*, 9, 389, and *Z. angew. Chem.*, 1897, 5.
[2] *Z. angew. Chem*, 1896, 549.
[3] Jones, *Am. J. Sci.*, [4] 7, 147 (1899).

If the solution does not contain sufficient glycerol the color change takes place too soon, as can be shown by the addition of more glycerol. If the red color disappears on adding the glycerol, more alkali is added until it reappears. The right end point is reached when the red color no longer disappears on the addition of glycerol. Inasmuch as commercial glycerol reacts acid, it must be just neutralized with alkali before being used for this determination. Furthermore, in order to obtain accurate results it is necessary that the solutions should be absolutely free from carbonate.

Application. Determination of Boric Acid in an Alkali Borate Free from Carbonate[1]

Dissolve about 30 g of the borate in water free from carbon dioxide, dilute to 1 l, and determine the total alkali in an aliquot part of 50 ml by titration with 0.5 N hydrochloric acid, in the presence of methyl red as indicator. Take another 50 ml of the borate solution and exactly neutralize by the amount of hydrochloric acid found necessary by the previous titration; by this means the solution will contain free boric acid. After adding about 50 ml of glycerol, 1 g of mannitol (cf. p. 518), or 50 ml of approximately 55 per cent invert sugar solution, titrate the solution with 0.1 N sodium hydroxide and phenolphthalein as indicator. When the end point is reached, add 10 ml more of glycerol; and this usually causes the solution to become colorless. Again add sodium hydroxide and repeat the process until finally the addition of glycerol causes no further action upon the end point.

If the borate contained carbonate, neutralize the portion taken for analysis with acid as before, then boil for a few minutes, taking the precaution of connecting the flask containing the solution with a return-flow condenser.[2] After the carbon dioxide is expelled, wash down the sides of the condenser with water and titrate with sodium hydroxide.

For the determination of boric acid in the presence of mineral acid,[3] add an excess of potassium iodide and iodate. The mineral acid reacts with the iodide-iodate mixture and sets free iodine (cf. p. 149), but boric acid does not do this. Discharge the iodine color with dilute sodium thiosulfate, added dropwise and avoiding an excess. Then add 1-2 g of mannitol and titrate with 0.1 N sodium hydroxide, with phenolphthalein as indicator.

If considerable mineral acid is present, neutralize the most of it with alkali hydroxide solution before adding the iodate-iodide mixture.

[1] M. Hönig and G. Spitz, Z. angew. Chem., 1896, 549.

[2] The condenser serves to keep back any boric acid escaping with the steam.

[3] Jones, loc. cit.

Determination of Boric Acid in Insoluble Silicates[1]

Fuse 0.5 g of a silicate such as glass with 3 g of Na_2CO_3 in a platinum crucible. Heat the mixture until the mass is liquid and continue heating for 2 or 3 minutes. Cool and treat the solid with 25 ml of water. Heat to gentle boiling, filter, and wash the residue with hot water until the last washings are nearly neutral to red litmus paper. Transfer the filtrate and washings to a 250-ml flask, add about 7 ml of concentrated HCl, heat nearly to boiling, and carefully add in small portions a slight excess of dry precipitated $CaCO_3$. Connect with a reflux condenser and boil for about 10 minutes. Filter, and wash the residue at least 8 times with hot water. Return the filtrate to the flask, add a little more $CaCO_3$, heat to boiling, and connect with a filter pump through a splash trap. Remove the flame and continue the suction until the boiling has nearly ceased. Cool to room temperature, filter if the residue is reddish, add phenolphthalein indicator, and slowly introduce 0.1 N NaOH from a buret until the indicator shows a pink color. Add 1 g of mannitol, shake, and continue titrating until the liquid is pink again. Add another gram of mannitol and more NaOH if necessary to impart a permanent color to the solution.

Remark. The method is excellent for routine control but the results are a little low because of the retention of borate in the residues.

13. Determination of Carbonic Acid

(a) Determination of Free Carbonic Acid

To determine the amount of free carbonic acid present in a dilute aqueous solution, add an excess of 0.1 N barium hydroxide solution, and determine the excess with 0.1 N HCl, with phenolphthalein as an indicator:

$$H_2CO_3 + Ba(OH)_2 = BaCO_3 + 2H_2O$$
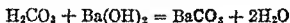
$$1 \text{ ml of } 0.1 \ N \ HCl = 0.0022 \text{ g } CO_2$$

(b) Determination of Carbon Dioxide Present as Bicarbonate

Titrate the solution with 0.1 N HCl in the presence of methyl orange:

$$NaHCO_3 + HCl = NaCl + H_2CO_3$$
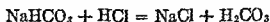
$$1 \text{ ml of } 0.1 \ N \ HCl = 0.0044 \text{ g } CO_2$$

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[1] Wherry and Chapin, *J. Am. Chem. Soc.*, **30**, 1687 (1908); Sullivan and Taylor, *J. Ind. Eng Chem.*, **6**, 897 (1914).

(c) Determination of Carbon Dioxide Present as Carbonate

Titrate with 0.1 N HCl and methyl orange:

$$Na_2CO_3 + 2HCl = 2NaCl + H_2CO_3$$
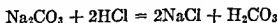
$$1 \text{ ml of } 0.1\ N \text{ HCl} = 0.0022 \text{ g } CO_2$$

Dissolve an alkaline-earth carbonate in an excess of 0.1 N acid and titrate back with 0.1 N acid.

(d) Determination of Free Carbonic Acid in the Presence of Bicarbonate

Titrate one portion with 0.1 N HCl and methyl orange as indicator, and determine the amount of bicarbonate as under (b).

Treat a second portion with an excess of barium chloride,[1] then with an excess of barium hydroxide, and titrate the excess of the hydroxide with HCl, with phenolphthalein as indicator. If the volume of 0.1 N acid used for the first titration is deducted from the volume of 0.1 N barium hydroxide solution found to be necessary in the last titration, the difference multiplied by 0.0022 will give the amount of free carbonic acid.[2]

(e) Determination of Alkali Bicarbonate in the Presence of Carbonate

See p. 498.

14. Determination of Carbonic Acid in the Air.   Method of Pettenkofer

Principle. A large, measured volume of air is treated with an excess of titrated barium hydroxide solution whereby the carbon dioxide is quantitatively absorbed, forming insoluble barium carbonate. Phenolphthalein is added, and the excess of barium hydroxide is determined by titration with hydrochloric acid until the solution is colorless. From the amount of base used to absorb the carbon dioxide, the amount of the latter is calculated, 1 ml of N Ba(OH)$_2$ = 0 022 g CO_2 = 11.13 ml of CO_2 gas at 0° and 760 mm pressure

Requirements. 1. A calibrated bottle of 5-l capacity.

2 Standard solutions of barium hydroxide and hydrochloric acid. Prepare the acid so that 1 ml = 0.25 ml CO_2 at 0°C and 760 mm pressure; this is accomplished by diluting 224.7 ml of 0 1 N hydrochloric acid to 1 l The barium hydroxide solution should be of about the same strength.

Procedure. Place the dry bottle, with its capacity etched upon it, in the space from which the air is to be taken; change the air in the bottle

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[1] The addition of barium chloride is necessary only when free carbonic acid is titrated in the presence of alkali bicarbonates. Without it free alkali would then be formed: NaHCO$_3$ + Ba(OH)$_2$ = BaCO$_3$ + H$_2$O + NaOH.

[2] This method cannot be used when magnesium salts are present.

CHAPTER XV

OXIDATION METHODS

Oxidation and reduction processes are those in which the substance analyzed is either oxidized or reduced by means of the solution with which the titration is made. When hydrogen is oxidized by oxygen it is changed from the neutral condition to that of a positive valence (or polarity) of 1 and oxygen is reduced from the neutral condition to a negative valence (or polarity) or 2. In this, and all other cases, the equivalent weight of the element used in an oxidation-reduction reaction is the atomic weight divided by the change in polarity. When an atom in any complex molecule is subjected to a change in polarity (oxidized or reduced) the equivalent weight of the compound is the gram-molecular weight divided by the *change in polarity* of the oxidized or reduced element. If more than 1 atom of the reactive element is present in the molecule, the molecular weight is divided by the total change in polarity, that is, by the change in polarity multiplied by the number of atoms undergoing such change (cf. p. 450).

Potassium dichromate is one of the well-known oxidizing agents used in volumetric analysis. It reacts, for example, with ferrous, stannous, or titanous salts and is reduced, thereby, to trivalent chromic salt. Equations for the reduction of the dichromate ion and oxidation of ferrous ion, etc., have been given on p. 450. Expressed in terms of electrons, e, the equation for the reduction of dichromate can be written

$$Cr_2O_7^{--} + 14H^+ + 6e = 2Cr^{+++} + 7H_2O$$

and that of the oxidation of ferrous ion

$$Fe^{++} - e = Fe^{+++}$$

These equations represent what actually takes place when the reduction of the dichromate is accomplished at the cathode and the oxidation of the iron is brought about at the anode of an electrolytic cell. There are 6.06×10^{23} actual atoms of iron in a gram atom, and if we multiply the actual charge of the electron by 6.06×10^{23} we obtain the value 96,500 coulombs which is called a *faraday*. When 6 faradays of electricity pass through an electrolytic cell containing an acid solution of dichromate at the cathode and a ferrous salt at the anode, 1 mole of dichromate can be reduced and 6 moles of ferrous iron can be oxidized.

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The above equations, therefore, show that the equivalent weight of dichromate is one-sixth of its molecular weight and that of ferrous ion is one atomic weight. The equation

$$Cr_2O_7^{--} + 6Fe^{++} + 14H^+ \rightarrow 2Cr^{+++} + 6Fe^{+++} + 7H_2O$$

represents six equivalent weights of both dichromate and iron.

The two following tables show the change in polarity of some of the more common oxidizing and reducing agents. In these tables M signifies the weight of 1 mole.

COMMON OXIDIZING AGENTS

Reagent	Polarity Change	Gain in Electrons*	Equivalent Weight
Cl_2	0 to -1	$2e$	$M/2$
Br_2	0 to -1	$2e$	$M/2$
I_2	0 to -1	$2e$	$M/2$
$K_2Cr_2O_7$	Cr^{VI} to Cr^{III}	$6e$	$M/6$
$KMnO_4$	Mn^{VII} to Mn^{++}	$5e$	$M/5$
$KMnO_4$	Mn^{VII} to Mn^{IV}	$3e$	$M/3$
$KBrO_3$	Br^V to Br^-	$6e$	$M/6$
KIO_3	I^V to I^-	$6e$	$M/6$
$KClO_3$	Cl^V to Cl^-	$6e$	$M/6$
Cu	Cu^{++} to Cu^+	$1e$	M
Na_2O_2	O_2^{--} to $2O^{--}$	$2e$	$M/2$
concd. HNO_3	N^V to NO_2	$1e$	M
HNO_3	N^V to NO	$3e$	$M/3$
H_2O_2	O_2^{--} to $2O^{--}$	$2e$	$M/2$

COMMON REDUCING AGENTS

Reagent	Polarity Change	Loss in Electrons	Equivalent Weight
$FeSO_4$ (or any ferrous salt)	Fe^{++} to Fe^{+++}	$1e$	M
$SnCl_2$	Sn^{II} to Sn^{IV}	$2e$	$M/2$
HI	I^- to I^o	$1e$	M
Zn	Zn^o to Zn^{++}	$2e$	$M/2$
H_2O_2	O_2^{--} to O_2^o	$2e$	$M/2$
H_2S	S^{-2} to S^o	$2e$	$M/2$
$C_2O_4^{--}$	$C_2O_4^{--}$ to $2CO_2$	$2e$	$M/2$
S_2O_3	$2S_2O_3^{--}$ to $S_4O_6^{--}$	$2e$	M of $Na_2S_2O_3$
$HAsO_2$	As^{III} to As^V	$2e$	$M/2$
SO_3	S^V to S^{VI}	$2e$	$M/2$
As_2O_3	As^{III} to As^V	$4e$	$M/4$
$TiCl_3$	Ti^{III} to Ti^{IV}	$1e$	M
Fe	Fe^o to Fe^{++}	$2e$	$M/2$
Fe dissolved in acid	Fe^{++} to Fe^{+++}	$1e$	M

* The letter e is used in this book to designate a milliequivalent and also, as in this table, to designate an electron. In oxidation-reduction reactions the milliequivalents are determined by the loss or gain of electrons as the table shows.

From these tables of equivalent weights it is easy to write equations and compute results. It is not necessarily true that there will be a definite reaction between any given reducing agent and any oxidizing agent. Thus the oxidation of $S_2O_3^{--}$ to $S_4O_6^{--}$ will go easily with iodine solution but does not take place in the same way with permanganate although permanganate can be standardized indirectly against thiosulfate by allowing the permanganate to liberate I_2 from KI in acid solution and titrating the liberated I_2 with thiosulfate. Under certain conditions, $HAsO_3^{--}$ can be oxidized to $HAsO_4^{--}$ by MnO_4^- in acid solution. The tables show that $HAsO_3/2$ and $MnO_4/5$ are equivalents; therefore,

$$5HAsO_3^{--} + 2MnO_4^- + 6H^+ \rightarrow 5HAsO_4^{--} + 2Mn^{++} + 3H_2O$$
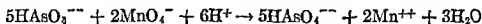
In such equations, when the oxidizer and reducer have been balanced and the proper products placed on the right-hand side of the equation, if there are then more positive charges on the right than on the left, add the requisite number of H^+ to the left side. If there are already more positive charges on the left, add water and form H^+ therefrom on the right. One must bear in mind, however, the conditions under which the reaction takes place and not form H^+ on the right if the solution is kept alkaline or use H^+ on the left if the solution is alkaline. In such cases OH^- can be formed on the right or added to the left side of the equation. Sometimes H_2O should be added to one side of the equation and H^+ or OH^- on the other.

ELECTROCHEMICAL THEORY OF OXIDATION-REDUCTION

Some of the reactions of acidimetry and alkalimetry are best understood by considering the ionization constants of the acids and bases and by applying the mass-action principle to the ionization of weak acids and bases. The strength of an acid, or of a base, can be expressed either in terms of these ionization constants or of the pH values of solutions of the same normal concentration. Thus if we were to take tenth-normal solutions of all acids and bases, measure the pH value of each of these solutions, and make a table arranging these acids and bases in order corresponding to increasing pH, we should find at the top of the table the strong mineral acids, HCl and HNO_3, with a pH of nearly 1 in tenth-normal solution, and at the bottom of the table the alkali hydroxides with a pH of nearly 13.

In such a table, we would find that the pH of a tenth-normal solution of an acid becomes larger as the ionization constant diminishes and the pH of a tenth-normal solution of a base becomes smaller as its ionization constant diminishes.

A salt of a weak acid added to a solution of a stronger acid raises the pH value; for example, we find that sodium acetate added to a solution of hydrochloric acid reduces the hydrogen-ion concentration and in that sense neutralizes the hydrochloric acid. When the difference in the ionization constants of two acids varies by about 10^4 it takes only a very small quantity of the stronger acid to furnish as many hydrogen ions as a fairly large quantity of the weaker acid does, and we can titrate all of the stronger acid before an appreciable quantity of the weaker acid reacts with the added base; if at some part of the solution some of the weaker acid is neutralized, the salt formed will at once enter into equilibrium with the hydrogen ions from the stronger acid, so that the final effect will be that only the strong acid is neutralized at the first end point.

In considering the reactions of oxidation-reduction it is useful to prepare a table to show the relative strengths of the various oxidizing and reducing agents. Just as all acids and bases can be classified in a common table on the basis of the pH values, so it is possible to prepare a single table which will show the tendency of each substance to undergo oxidation or reduction. Such a table can be called a *potential series*. It has been called a table of *oxidation potentials*. Just as we could use the concentration of OH^- as a basis of comparing dilute solutions of acids and bases instead of the concentration of H^+, because the product $[H^+] \times [OH^-]$ is equal to 10^{-14} in every solution at room temperature, so we can call the table one of *reduction potentials* since oxidation is just the opposite to reduction and all we have to do is to change the sign. In some textbooks, the same table is called one of *electrode potentials*. Whatever the table may be called, it is customary to place the strong reducing agents at the top of the list and end with the strong oxidizing agents. Thus, in considering the free elements with respect to their tendencies to undergo oxidation or reduction, we place the alkali metals at the top and the non-metal oxygen followed by fluorine at the bottom.

It has already been pointed out that a substance is said to be oxidized or reduced when some atom it contains has undergone a change in polarity. Oxidation results when the polarity is increased, and reduction when the polarity is decreased. In terms of the electron theory, an increase in polarity means the loss of one or more electrons by an atom. Our definition of oxidation, therefore, has lost its original significance of necessarily having something to do with oxygen. The atom of oxygen is believed to consist of a nucleus around which eight electrons are circulating, probably in elliptical orbits. The path of the first two electrons, like that of the electrons around the helium nucleus, lies closer to the nucleus than that of the other six electrons, and we say that oxygen belongs in Family VI of the periodic table. When oxygen enters

into combination with another element to form an oxide other than a peroxide, it accepts two electrons from the other element. Even if there is no ionization of the oxide molecule, it is reasonable to assume that the oxygen is negative with respect to the other element and that it has become negative by receiving electrons. Thus, in the water molecule, we are accustomed to think of the hydrogen as being positive to the oxygen although the electron of each hydrogen atom may be merely shared with the oxygen. Whenever, therefore, any atom gives up one or more of its electrons to some other atom, or even if it merely shares one or more of its electrons with some other atom, the atom to which the electron or electrons originally belonged is said to be oxidized and the element offered the electron is said to be reduced.

This electronic conception of oxidation and reduction makes it easy to see why an oxidation is always accompanied by a reduction. A transfer of electrons takes place whenever an electric current flows through an aqueous solution containing an electrolyte. At the anode, where electrons pass from the solution to the wire, some substance is oxidized. This oxidation may be the liberation of oxygen gas, the liberation of halogen gas, the dissolving of a metal electrode, the deposition of a higher oxide such as PbO_2 or MnO_2 upon the anode, or the oxidation of some substance present in the electrolyzed solution such as a ferrous salt. At the same time that an oxidation takes place at the anode, electrons enter the solution at the cathode and a reduction takes place. This reduction may be the deposition of copper upon the cathode, the liberation of hydrogen gas, or the reduction of some substance in solution such as ferric salt, permanganate, or chromate. The only difference between oxidation and reduction of a titration and that of an electrolysis is that the reactions take place side by side in a titration and at some distance apart during electrolysis. Moreover, a chemical reaction of oxidation-reduction can be used as a source of an electric current, as will be explained.

If we place a piece of zinc in a solution of zinc sulfate and a piece of copper in a solution of copper sulfate and connect the two solutions by means of an inverted U-tube containing ammonium chloride solution, there will be no appreciable reaction until the copper and zinc are connected by a wire outside the solutions. Then a current will flow, electrons will pass from the wire to the solution and deposit copper, and electrons will leave the zinc and pass to the wire, forming zinc ions in the solution. The zinc, according to our definition, is oxidized and the copper is reduced; the two reactions take place simultaneously, and the effect is the same as if the piece of zinc were placed directly in the copper sulfate solution except that then we would not get any evidence

of an electric current. In precisely the same way we can produce an electric current by making use of the reaction between potassium dichromate and some substance that it oxidizes, such as hydrogen sulfide or ferrous chloride. To get the electric current in a wire, we must place the acid solution of dichromate in one vessel and the hydrogen sulfide or ferrous salt in another. We must provide some indifferent electrolyte between the two solutions, and place an insoluble electrode in each solution. Then, as soon as the electrodes are connected by a wire, a current will flow. The dichromate will be reduced in one vessel and the hydrogen sulfide or ferrous salt will be oxidized in the other, and the final effect will be exactly the same as if the dichromate solution were added directly to the solution of the ferrous salt.

The potential series of the elements, therefore, can be expanded to include almost every reaction of oxidation or reduction, although, to be sure, it is sometimes difficult to measure the electrode potentials and many of them are not known with any degree of exactness. The measurement of the potentials is usually accomplished by measuring the potential difference between two electrodes of which one is a standard half-cell of definitely known potential.

These potentials enable one to predict whether a given oxidation is likely to take place to completion so that it can be used in quantitative analysis. They do not tell, however, whether the speed of the reaction is sufficiently high to make the process satisfactory. Thus permanganate should be able to oxidize the reduced forms of substances listed about 0.15 volt higher in the table, but often the reaction takes place too slowly, as in the reaction with oxalic acid at room temperature. The presence of a catalyst is often needed.

The mass-action law applies to every oxidation-reduction reaction, and it is important that the beginner should understand this application. The potential of a metal against a solution of its ions is governed by the mathematical expression

$$E_{30} = E_0 + \frac{0.060}{n} \log c$$

when E_{30} is the observed electrode potential at 30°, E_0 is the potential given in the table (corresponding to the potential of the metal in a molal solution of its ions), n is the change in polarity, and c is the concentration of the ions expressed in moles per liter. The value 0.060 is a constant which varies with the absolute temperature; at 25° it is 0.059 and at 18° it is 0.058. The equation shows that the observed oxidation potential grows smaller by 0.060 volt for a change of valence of one, or 0.030 volt for

a valence change of two, when the concentration of the ions in the solution is 0.1 molal instead of molal. This means that the metal is easier to oxidize when the solution does not contain many of its ions and harder to deposit by electrolysis.

The student may notice that the above equation is sometimes written with a negative sign on the right-hand side. It is a purely arbitrary decision whether a given potential is called positive or negative with respect to hydrogen, and depends entirely on the definition of what is meant by *positive*. The chemist usually thinks of the elements at the top of the column as positive elements, but in making up an electrolytic cell, the positive-to-negative direction of the current *in the wire* is always from the lower to the higher member of the series. Thus, in the Daniell cell, the physicist considers the zinc immersed in zinc sulfate solution the negative element and the copper immersed in copper sulfate solution the positive element. Zinc is positive to copper in the solution, and copper is positive to zinc in the wire. When the signs are changed the *oxidation* potential becomes the *reduction* potential. With reduction potentials the above equation becomes

$$E_{20} = E_0 - \frac{0.060}{n} \log c \quad \text{or} \quad E_{20} = E_0 + \frac{0.060}{n} \log \frac{1}{c}$$

The following table gives the oxidation potentials of some of the common substances which easily undergo oxidation or reduction. Some of the potentials are not known exactly, but the relative position in the table is right in most cases. The values of E_0 apply when the concentrations of both the oxidized and reduced forms are equal to 1 molal. If the hydrogen ion enters into the reaction, the values correspond to the presence of sufficient hydrogen ions to make the solution molal. The concentration of water is assumed to be constant and not changed appreciably by the progress of the reaction. The letter e in the equilibrium expressions represents a "gram electron" or electricity corresponding to 1 faraday = 96,500 coulombs or 26.82 ampere-hours.

The electrode reaction for a simple case of oxidation-reduction in which no other substance participates can be written

$$\text{Ox} + n \, e \rightleftarrows \text{Red}$$
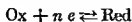
when Ox represents one mole of the oxidized form, Red one mole of the reduced form, n the change in polarity, and e the electron (faraday in case of the gram atom). The equilibrium between a metal and its ions is a special case in which the metal represents the reduced form, and since the metal as such is insoluble in water, its concentration does not enter into consideration. The equilibrium is the same whether we take a wire or a thick rod of the metal. If, however, the substance exists to an appreciable extent dissolved in the solution, the concentration of both Ox and Red has an effect upon the final state of equilib-

NORMAL OXIDATION POTENTIALS

Oxidized Form	Reduced Form	Change in Polarity	Electrode Reaction	Normal Potential or E_0 in Volts
Li^+	Li	1	$Li^+ + e \rightleftharpoons Li$	−3.02
Rb^+	Rb	1	$Rb^+ + e \rightleftharpoons Rb$	−2.93
K^+	K	1	$K^+ + e \rightleftharpoons K$	−2.92
Sr^{++}	Sr	2	$Sr^{++} + 2e \rightleftharpoons Sr$	−2.92
Ba^{++}	Ba	2	$Ba^{++} + 2e \rightleftharpoons Ba$	−2.9
Ca^{++}	Ca	2	$Ca^{++} + 2e \rightleftharpoons Ca$	−2.7
Na^+	Na	1	$Na^+ + e \rightleftharpoons Na$	−2.7
Mg^{++}	Mg	2	$Mg^{++} + 2e \rightleftharpoons Mg$	−2.40
Al^{+++}	Al	3	$Al^{+++} + 3e \rightleftharpoons Al$	−1.7
Be^{++}	Be	2	$Be^{++} + 2e \rightleftharpoons Be$	−1.69
U^{++++}	U	4	$U^{++++} + 4e \rightleftharpoons U$	−1.4
Mn^{++}	Mn	2	$Mn^{++} + 2e \rightleftharpoons Mn$	−1.1
H_2O	$\frac{1}{2}H_2$	1	$H_2O + e \rightleftharpoons \frac{1}{2}H_2 + OH^-$	−0.83
Zn^{++}	Zn	2	$Zn^{++} + 2e \rightleftharpoons Zn$	−0.76
Cr^{++}	Cr	2	$Cr^{++} + 2e \rightleftharpoons Cr$	−0.56
S	S^{--}	2	$S + 2e \rightleftharpoons S^{--}$	−0.55
Ga^{+++}	Ga	3	$Ga^{+++} + 3e \rightleftharpoons Ga$	−0.5
Fe^{++}	Fe	2	$Fe^{++} + 2e \rightleftharpoons Fe$	−0.43
Cr^{+++}	Cr^{++}	1	$Cr^{+++} + e \rightleftharpoons Cr^{++}$	−0.4
Cd^{++}	Cd	2	$Cd^{++} + 2e \rightleftharpoons Cd$	−0.4
In^{+++}	In	3	$In^{+++} + e \rightleftharpoons In$	−0.38
Tl^+	Tl	1	$Tl^+ + e \rightleftharpoons Tl$	−0.34
Co^{++}	Co	2	$Co^{++} + 2e \rightleftharpoons Co$	−0.29
Ni^{++}	Ni	2	$Ni^{++} + 2e \rightleftharpoons Ni$	−0.23
SbO^+	Sb	3	$SbO^+ + 2H^+ + 3e \rightleftharpoons Sb + H_2O$	−0.21
V^{+++}	V^{++}	1	$V^{+++} + e \rightleftharpoons V^{++}$	−0.2
CO_2	$\frac{1}{2}H_2C_2O_4$	1	$CO_2 + H^+ + e \rightleftharpoons \frac{1}{2}H_2C_2O_4$	−0.2?
Sn^{++}	Sn	2	$Sn^{++} + 2e \rightleftharpoons Sn$	−0.14
Pb^{++}	Pb	2	$Pb^{++} + 2e \rightleftharpoons Pb$	−0.12
CbO_3^-	Cb^{+++}	2	$CbO_3^- + 6H^+ + 2e \rightleftharpoons Cb^{+++} + H_2O$	−0.1?
H^+	$\frac{1}{2}H_2$	1	$H^+ + e \rightleftharpoons \frac{1}{2}H_2$	−0.00
SO_4^{--}	S^-	8	$SO_4^{--} + 8H^+ + 6e \rightleftharpoons S + 4H_2O$	?
H_2MoO_4	Mo^{+++}	3	$H_2MoO_4 + 6H^+ + 3e \rightleftharpoons Mo^{+++} + 3H_2O$	0.0?
Ti^{++++}	Ti^{+++}	1	$TiO^{++} + e \rightleftharpoons Ti^{+++}$	+0.04
TiO^{++}	Ti^{+++}	1	$TiO^{++} + 2H^+ + e \rightleftharpoons Ti^{++++} + H_2O$	+0.04
WO^{+++}	W^{++++}	1	$WO^{+++} + 2H^+ + e \rightleftharpoons W^{++++} + H_2O$	+0.1?
$\frac{1}{2}S_4O_6^{--}$	$S_2O_3^{--}$	1	$\frac{1}{2}S_4O_6^{--} + e \rightleftharpoons S_2O_3^{--}$	+0.13
SO_4^{--}	H_2SO_3	2	$SO_4^{--} + 4H^+ + 2e \rightleftharpoons H_2SO_3 + H_2O$	+0.14
Sn^{++++}	Sn^{++}	2	$Sn^{++++} + 2e \rightarrow Sn^{++}$	+0.14
S°	H_2S	2	$S^\circ + 2H^+ + 2e \rightarrow H_2S$	+0.17
Bi^{+++}	Bi	3	$Bi^{+++} + 3e \rightleftharpoons Bi$	+0.2
$[PtCl_4]^{--}$	Pt	2	$[PtCl_4]^{--} + 2e \rightarrow Pt + 4Cl^-$	+0.2

NORMAL OXIDATION POTENTIALS — *Continued*

Oxidized Form	Reduced Form	Change in Polarity	Electrode Reaction Form	Normal Potential or E_0 in Volts
Sb^{+++}	Sb	3	$Sb^{+++}+3e \rightleftarrows Sb$	$+0.2$
$AgCl$	Ag^+	1	$AgCl+e \rightleftarrows Ag^+ +Cl^-$	$+0.23$
V^{+++}	V^{++}	1	$V^{+++}+e \rightarrow V^{++}$	-0.2
			Normal calomel electrode at 25°	$+0.285$
As^{+++}	As	3	$As^{+++}+3e \rightleftarrows As$	$+0.3$
(H_2WO_4)	WO^{+++}	1	$H_2WO_4+4H^+ +e \rightleftarrows WO^{+++}+3H_2O$	$+0.3?$
			Decinormal calomel electrode at 25°	$+0.338$
Cu^{++}	Cu	2	$Cu^{++}+2e \rightleftarrows Cu$	$+0.34$
UO_2^{++}	U^{++++}	2	$UO_2^{++}+4H^+ +2e \rightleftarrows U^{++++}+2H_2O$	$+0.36$
$\frac{1}{2}O_2$	OH^-	2	$\frac{1}{2}O_2+H_2O+2e \rightleftarrows 2OH^-$	$+0.40$
$[PtCl_4]^{--}$	$[PtCl_4]^{----}$	2	$[PtCl_6]^{--}+2e \rightleftarrows [PtCl_4]^{----}+2Cl^-$	$+0.47$
VO^+	V^{+++}	1	$VO^+ +2H^+ +e \rightleftarrows V^{+++}+H_2O$	$+0.4$
HVO_2	V^{++}	3	$HVO_2+H^+ +3e \rightleftarrows V^{++}+3H_2O$	$+0.47$
Cu^{++}	$CuCl_2^-$	1	$Cu^{++}+2Cl^- +e \rightleftarrows CuCl_2^-$	$+0.46$
H_2SO_3	S	4	$H_2SO_3+4H^+ +4e \rightleftarrows S+3H_2O$	$+0.47$
$Fe(CN)_6^{---}$	$Fe(CN)_6^{----}$	1	$Fe(CN)_6^{---}+e \rightleftarrows Fe(CN)_6^{----}$	$+0.49$
CO_2	$C_2O_4^{--}$	1	$2CO_2+2e \rightleftarrows C_2O_4^{--}$	?
H_2MoO_4	MoO^{+++}	1	$H_2MoO_4+4H^+ +e \rightleftarrows MoO^{+++}$ $+3H_2O$	$+0.5$
			Methylene blue at pH 2.86	$+0.53$
$\frac{1}{2}I_2$	I^-	1	$\frac{1}{2}I_2+e \rightleftarrows I^-$	$+0.54$
H_3SbO_4	H_3SbO_3	2	$\begin{cases} H_3SbO_4+5H^+ +2e \rightleftarrows Sb^{+++}+4H_2O \\ H_3SbO_4+H_2O+2e \leftarrow H_3SbO_3+2OH^- \end{cases}$	?
H_3AsO_4	H_3AsO_3	2	$H_3AsO_4+2H^+ +2e \rightleftarrows H_3AsO_3+H_2O$	$+0.57$
MnO_4^-	MnO_2	3	$MnO_4^- +2H_2O+3e \rightarrow MnO_2+4OH^-$	$+0.59$
MnO_4^-	MnO_4^{--}	1	$MnO_4^- +e \rightleftarrows MnO_4^{--}$	$+0.66$
HNO_2	NO	1	$NO_2^- +2H^+ +e \rightleftarrows NO+H_2O$	$+0.77$
$C_6H_4O_2$	$C_6H_4(OH)_2$	2	$C_6H_4O_2+2H^+ +2e \rightarrow C_6H_4(OH)_2$ quinhydrone electrode	$+0.70$
H_2SeO_3	Se	4	$H_2SeO_3+4H^+ +4e \rightleftarrows Se+3H_2O$	$+0.74$
Fe^{+++}	Fe^{++}	1	$Fe^{+++}+e \rightleftarrows Fe^{++}$	$+0.75$
$\frac{1}{2}Hg_2^{++}$	Hg^+	1	$\frac{1}{2}Hg_2^{++}+e \rightleftarrows Hg$	$+0.80$
Ag^+	Ag	1	$Ag^+ +e \rightleftarrows Ag$	$+0.80$
Pd^{++}	Pd	2	$Pd^{++}+2e \rightleftarrows Pd$	$+0.82$
Hg^{++}	Hg	2	$Hg^{++}+2e \rightleftarrows Hg$	$+0.86$
Hg^{++}	$\frac{1}{2}Hg_2^{++}$	1	$Hg^{++}+e \rightleftarrows \frac{1}{2}Hg_2^{++}$	$+0.90$
HVO_3	VO^{++}	1	$VO_3^- +4H^+ +e \rightleftarrows VO^{++}+2H_2O$	$+0.92$
Dil. HNO_3	HNO_2	2	$NO_3^- +2H^+ +2e \rightleftarrows NO_2^- +H_2O$	$+0.9$
Conc. HNO_3	NO_2	1	$NO_3^- +2H^+ +2e \rightleftarrows NO_2+H_2O$	?
$\frac{1}{2}Br_2$	Br^-	1	$\frac{1}{2}Br_2+e \rightleftarrows Br^-$	$+1.07$
O_2	H_2O_2	2	$O_2+2H^+ +2e \rightleftarrows H_2O_2$	$+1.08$
IO_3^-	I^-	6	$IO_3^- +6H^+ +6e \rightleftarrows I^- +3H_2O$	$+1.09$

NORMAL OXIDATION POTENTIALS — Continued

Oxidized Form	Reduced Form	Change in Polarity	Electrode Reaction Form	Normal Potential or E_0 in Volts
H_2SeO_4	H_2SeO_3	2	$H_2SeO_4 + 2H^+ + 2e \rightarrow H_2SeO_3 + H_2O$	+1.09
$Cr_2O_7^{--}$	$2Cr^{+++}$	6	$Cr_2O_7^{--} + 14H^+ + 6e \rightleftarrows 2Cr^{+++} + 7H_2O$	+1.195
IO_3^-	$\frac{1}{2}I_2$	5	$IO_3^- + 6H^+ + 5e \rightleftarrows \frac{1}{2}I_2 + 3H_2O$	+1.20
Au^{+++}	Au^+	2	$Au^{+++} + 2e \rightleftarrows Au^+$	+1.2
$\frac{1}{2}O_2$	H_2O	2	$\frac{1}{2}O_2 + 2H^+ + 2e \rightleftarrows H_2O$	+1.23
MnO_2	Mn^{++}	2	$MnO_2 + 4H^+ + 2e \rightleftarrows Mn^{++} + 2H_2O$	+1.33
ClO_4^-	Cl^-	8	$ClO_4^- + 8H^+ + 8e \rightleftarrows Cl^- + 4H_2O$	+1.35
$\frac{1}{2}Cl_2$	Cl^-	1	$\frac{1}{2}Cl_2 + e \rightleftarrows Cl^-$	+1 36
Au^{+++}	Au	3	$Au^{+++} + 3e \rightleftarrows Au$	+1.36
BrO_3^-	Br^-	6	$BrO_3^- + 6H^+ + 6e \rightleftarrows Br^- + 3H_2O$	+1.42
Ce^{++++}	Ce^{+++}	1	$Ce^{++++} + e \rightleftarrows Ce^{+++}$	+1 45
ClO_3^-	Cl^-	6	$ClO_3^- + 6H^+ + 6e \rightleftarrows Cl^- + 3H_2O$	+1.45
BrO_3^-	Br^-	6	$BrO_3^- + 6H^+ + 6e \rightleftarrows Br^- + 3H_2O$	+1.48
BrO_3^-	$\frac{1}{2}Br_2$	5	$BrO_3^- + 6H^+ + 5e \rightleftarrows \frac{1}{2}Br_2 + 3H_2O$	+1.49
Au^+	Au	1	$Au^+ + e \rightleftarrows Au$	+1.5
MnO_4^-	Mn^{++}	5	$MnO_4^- + 8H^+ + 5e \rightleftarrows Mn^{++} + 4H_2O$	+1.52
MnO_4^-	MnO_2	3	$MnO_4^- + 4H^+ + 3e \rightleftarrows MnO_2 + 2H_2O$	+1.58
$S_2O_8^{--}$	$2SO_4^{--}$	2	$S_2O_8^{--} + 2e \rightleftarrows 2SO_4^{--}$	?
PbO_2	$PbSO_4$	2	$PbO_2 + 4H^+ + SO_4^{--} + 2e \rightarrow PbSO_4 + 2H_2O$	+1.68
Co^{+++}	Co^{++}	1	$Co^{+++} + e \rightleftarrows Co^{++}$	+1.82
IO_4^-	IO_3^-	2	$IO_4^- + 2H^+ + 2e^- \rightleftarrows IO_3^- + H_2O$	?
H_2O_2	H_2O	2	$H_2O_2 + 2H^+ + 2e \rightleftarrows 2H_2O$	+1.9
$NaBiO_3$	Bi^{+++}	2	$NaBiO_3 + 6H^+ + 2e \rightarrow Na^+ + Bi^{+++} + 3H_2O$	?
$\frac{1}{2}F_2$	F^-	1	$\frac{1}{2}F_2 + e \rightleftarrows F^-$	+2.8

rium. With these concentrations in moles per liter expressed as [Ox] and [Red], the expression for the normal potential becomes

$$E_{20} = E_0 + \frac{0.060}{n} \log \frac{[Ox]}{[Red]}$$

The value E_0 is that given in the table where it is assumed that each concentration is that of n molal solution. Then since [Ox] = [Red] and the log of 1 = 0, the second term disappears and $E_{20} = E_0$.

If hydrogen or hydroxide ions take part in the reaction they also influence the final state of equilibrium. Thus, in the reaction $H_3AsO_4 + 2H^+ + 2e \rightleftarrows H_3AsO_3 + H_2O$, the potential is determined by the

equation:

$$E_{30} = E_0 + \frac{0.060}{2} \log \frac{[H_3AsO_4][H^+]^2}{[H_2AsO_3]}$$

and in the reaction $MnO_4^- + 8H^+ + 5e \rightleftarrows Mn^{++} + 4H_2O$ the potential is determined by the equation

$$E_{30} = E_0 + \frac{0.060}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{++}]}$$

In these last two equations it is not necessary to take the H_2O into consideration because when the reaction takes place in a dilute solution the concentration of the water does not change appreciably as a result of the progress of the oxidation and reduction. The concentration of the hydrogen ions determines the final state of equilibrium to a marked degree in the above reactions. Thus, in a strongly acid solution, arsenic acid can be reduced quantitatively to arsenious acid by means of potassium iodide, but in a slightly alkaline solution, arsenite can be oxidized completely to arsenate by iodine. The above arsenate-arsenite equation can be written

$$E_{30} = E_0 + \left[\frac{0.060}{2} \log \frac{[H_3AsO_4]}{[H_3AsO_3]} + \frac{0.060}{2} \log [H]^2 \right]$$

and in this form can be used to calculate the effect of changes in hydrogen-ion concentration or to calculate the effect of changes in the $[H_3AsO_4]$ to $[H_3AsO_3]$ ratio at a definite concentration of hydrogen ions.

With permanganate, the reduction products are different at different concentrations of hydrogen ions. Thus in acid solutions, Mn^{++} is the usual product; in neutral or slightly alkaline solutions MnO_2 is usually formed; and in strongly alkaline solutions green MnO_4^{--} is sometimes obtained.

A. POTASSIUM PERMANGANATE METHODS

Manganese, from the standpoint of oxidation-reduction reactions, is an interesting element. The potentials relating to the various valence states are given in the following table:

REACTION	VOLTS
(a) $Mn = Mn^{++} + 2e$	-1.1
(b) $MnO_2 + 4OH^- = MnO_4^{--} + 2H_2O + 2e$	$+0.57$
(c) $MnO_2 + 4OH^- = MnO_4^- + 2H_2O + 3e$	$+0.59$
(d) $MnO_4^{--} = MnO_4^- + e$	$+0.66$
(e) $Mn^{+++} + 2H_2O = MnO_2 + 4H^+ + e$	$+1.2$
(f) $Mn^{++} + 2H_2O = MnO_2 + 4H^+ + 2e$	$+1.33$
(g) $Mn^{++} = Mn^{+++} + e$	$+1.5$
(h) $Mn^{++} + 4H_2O = MnO_4^- + 8H^+ + 5e$	$+1.52$
(i) $MnO_2 + 2H_2O = MnO_4^- + 4H^+ + 3e$	$+1.63$

In the table, the letter e signifies the electron, or the transfer of 1 faraday (96,500 coulombs) if the gram atom or gram molecule is understood. Black-faced type signifies that the substance as such is insoluble

The formation of a manganous salt from metallic manganese is indicated by equation (a). The normal potential of -1.1 volts indicates that the metal is oxidized a little more easily than zinc and somewhat less readily than aluminum (which is unprotected by an oxide film). Dilute acids, therefore, dissolve the metal with the evolution of hydrogen and the formation of bivalent manganous ions. Nitric acid, aqua regia, or halogens in the presence of a strong acid are incapable of oxidizing the manganous salt. The bivalent manganous salts, although slightly colored in the form of hydrated crystals, yield colorless solutions.

Salts of trivalent manganese, called manganic salts, are known but they are not very stable. Equation (e) shows that it is possible under some conditions to form a manganic salt from manganese dioxide and leads one to expect that it ought to be possible to oxidize a manganic salt to manganese dioxide in the presence of alkali hydroxide or the salt of a weak acid, because, since hydrogen ions are liberated when manganic salt is oxidized, the reaction should take place more readily if the hydrogen ions are removed as fast as they are formed. The potential of reaction (g) in the table indicates that manganic salts are easily reduced to manganous salts.

Some salts of quadrivalent manganese are known. Thus, cold concentrated hydrochloric acid will slowly dissolve manganese dioxide, forming manganese tetrachloride. Complex salts, such as K_2MnF_6 and K_2MnCl_6, have been prepared These salts, however, are not stable and are of little interest to the analytical chemist. The dioxide, MnO_2, occurs in nature as the mineral pyrolusite, which is the most important source of all manganese compounds and can be regarded as the anhydride of manganous acid, H_2MnO_3, which is known to have salts called manganites The potential of reaction (c) in the above table indicates that it ought to be possible to form MnO_4^- from MnO_2, and conversely that MnO_2 can be expected to be formed as a reduction product when permanganate acts as an oxidizer. Potassium permanganate is much used for the oxidation of many organic compounds in neutral or alkaline solutions, and MnO_2 is the reduction product that is usually formed. The potential of reaction (b) shows that MnO_2 in alkaline solution should be convertible into a manganate, such as Na_2MnO_4. All manganese oxides, on being fused with caustic alkali or alkali carbonate in the air or in the presence of some oxidizing agent such as potassium nitrate, are converted into green alkali manganate, and this reaction has frequently been used as a sensitive test for manganese. Usually the precipitate of manganous hydroxide produced by adding sodium hydroxide to the solution of a manganous salt is fused with sodium carbonate on platinum, and if the melt assumes a green color, the presence of manganese is indicated. The potential of reaction (f) shows that manganese dioxide is a good oxidizing agent, and this corresponds to the fact that we can dissolve it by treating with acid and any good reducing agent, such as a ferrous salt, an oxalate, a sulfite, or hydrogen peroxide. With hot concentrated hydrochloric acid, chlorine is formed.

$$MnO_2 + 2Fe^{++} + 4H^+ = Mn^{++} + 2Fe^{+++} + 2H_2O$$
$$MnO_2 + C_2O_4^{--} + 4H^+ = Mn^{++} + 2CO_2 + 2H_2O$$
$$MnO_2 + H_2O_2 + 2H^+ = Mn^{++} + O_2 + 2H_2O$$
$$MnO_2 + 2HCl = MnCl_2 + Cl_2$$
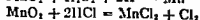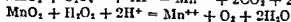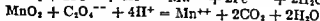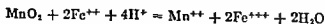
Aside from its characteristic color and use as a qualitative test, the green manganate anion MnO_4^{--} is of little interest to the analytical chemist. Equations (b) and (c), however, show that the oxidation potential of the manganate anion is close

to that of the permanganate anion. Sometimes, in the analysis of duplicate samples, the chemist finds after an oxidation treatment that one sample is green, showing the presence of manganate, and the other is purple owing to the formation of permanganate.

Permanganate ions, MnO_4^-, have such a strong color that a single drop of a tenth-normal permanganate solution will impart a perceptible color to 500 ml of another solution. Permanganate, therefore, is its own indicator. In most oxidations with permanganate that take place in acid solutions, the permanganate anion is reduced to colorless manganous cations and the reduction potential of the permanganate under those conditions is shown by equation (h) in the table on p. 534. In a nearly neutral solution, however, permanganate is capable of oxidizing manganous ions to the quadrivalent state, to which it is itself reduced. This is the so-called *Volhard* titration.

$$3Mn^{++} + 2MnO_4^- + 2H_2O = 5MnO_2 + 4H^+$$
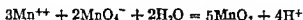
The potential values given on p. 534 should not be regarded as absolutely accurate. The measurement of some of these potentials is difficult, and sometimes it is hard to prevent some side reaction from taking place. The work performed in any chemical reaction of oxidation-reduction can be measured in joules or watt-seconds, that is, by multiplying the quantity of electricity involved by the voltage shown. If manganese from any valence is converted into manganese at some other valence, the work performed is theoretically the same whether the oxidation takes place all at once or in several stages. This enables one to compute some of the potential values in the table on p. 534 from other values that are given. In making such computations, the signs before the voltages in the table merely indicate which direction the current is moving; it is purely arbitrary whether the signs are made positive or negative (cf. p. 530). To show how computations can be made, the following illustration will serve:

Reaction (f) on p. 534 represents the oxidation of bivalent manganese to the quadrivalent state. Reaction (i) covers the oxidation of quadrivalent manganese to the septavalent state, and reaction (h) the oxidation of bivalent manganese directly to the septavalent state. In other words, reaction (h) represents the sum of reactions (f) and (i), and the work done is theoretically the same whether the reaction takes place in the two stages or all at once.

Energy is composed of two factors, an intensity factor and a capacity factor. The work done is measured by the product of these two factors   Thus, in measuring the work done in compressing a gas, we must take into consideration the change in volume (capacity factor) and the pressure (intensity factor), and the work done is measured by multiplying the pressure by the volume. In electrical units, the work done is measured by multiplying the amount of electricity moving (expressed in coulombs, ampere-seconds, or ampere-hours, etc.) and the potential difference (expressed in volts). In all the reactions given in the table on p. 534, therefore, the work done, or, as it is sometimes expressed, the change in the *free energy*, is proportional to the number of electrons liberated multiplied by the voltage shown. Thus in equation (a) the work done is proportional to the product 2×1.1. In the oxidation of a gram atom of manganese from the metallic to the manganous state, 2 faradays of electricity ($2 \times 96,500$ coulombs or ampere-seconds or 2×26.82 ampere-hours) are involved, and the potential drop is 1.1 volt.

Then, with respect to equations (f), (i), and (h) in the table on p. 534, if we call the

respective voltages v_1, v_2, and v_3, we have

$$2v_1 + 3v_2 = 5v_3$$

and if two of these values are known, the third can be computed. In such computations, it should be borne in mind that none of the values given in the table is to be regarded as absolutely correct. Whatever errors there may be in the values given for v_1, v_2, and v_3 are multiplied by 2, 3, and 5, respectively, so that the result of the calculation may differ a little from the value given. Thus

$$2 \times 1.33 + 3 \times 1.63 = 7.55$$

but 5 times the value given for v_3 in the table is $5 \times 1.52 = 7.60$, and this is as near as such computations can be expected to check. In this particular case, it is well to note that reaction (h) is the sum of reactions (f) and (i) and not the sum of reactions (c) and (f). Reaction (c) is very similar to reaction (i) but refers to a solution which is normal in OH^- whereas (i) refers to one which is normal in H^+.

When potassium permanganate acts as an oxidizing agent in distinctly acid solution, the manganese is reduced from a positive valence of 7 to a positive valence of 2 and the manganese atom accepts 5 electrons from the substance oxidized:

$$MnO_4^- + 8H^+ + 5e = Mn^{++} + 4H_2O$$

The equivalent weight of potassium permanganate, or the quantity required to make 1 l of normal solution, is, therefore, one-fifth of the molecular weight. In many reactions which take place in neutral or alkaline solutions, a precipitate of manganese dioxide is formed corresponding to a reduction to the quadrivalent state, but, since a solution of potassium permanganate is usually standardized in acid solution with complete reduction of the manganese to the bivalent state, it is customary to express the normality of permanganate on this basis.

The following equations represent the action of permanganate on some of the common substances which are oxidized quantitatively by it:

$$MnO_4^- + 5Fe^{++} + 8H^+ = Mn^{++} + 5Fe^{+++} + 4H_2O$$
$$2MnO_4^- + 5C_2O_4^{--} + 16H^+ \rightarrow 2Mn^{++} + 10CO_2 + 8H_2O$$
$$2MnO_4^- + 5Sn^{++} + 16H^+ \rightarrow 2Mn^{++} + 5Sn^{++++} + 8H_2O$$
$$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{++} + 5I_2 + 8H_2O$$
$$2MnO_4^- + 3Mn^{++} + 2H_2O \rightarrow 5MnO_2 + 4H^+$$
$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{++} + 8H_2O + 5O_2 \uparrow$$
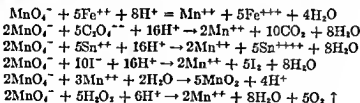
Preparation of Tenth-Normal Permanganate Solution

Weigh out on a watch glass approximately 3.2 g of potassium permanganate crystals and dissolve in 1 l of water. Boil the solution 10–15 minutes, allow to stand over night, or longer, and filter through asbestos.

For filtering the permanganate solution a thin asbestos felt on top of some glass wool in an ordinary funnel is satisfactory, and with such a filter no suction is needed. This is better than a Gooch filter, as contact of the permanganate solution with rubber will cause the formation of MnO_2, and $KMnO_4$ solution containing MnO_2 is always unstable.

The end point in a permanganate titration is easily obtained because 1 drop of the permanganate in excess imparts a distinct pink color to the solution. In permanganate work, therefore, there is not so much danger of running over the end point as with dichromate titrations and it is not necessary to have a solution on hand to titrate back with when the end point is overstepped. Many analyses, however, are accomplished by adding a measured volume of reducing agent of known strength and titrating the excess with permanganate. A solution of a ferrous salt is the commonest reducing agent thus used, but, as it oxidizes slowly on standing, its strength must be determined every day that it is used. A *pure* permanganate solution will keep indefinitely provided that it is kept in the dark, free from dust and reducing vapors. Ordinary distilled water, unless permanganate was present in the boiler, contains traces of organic material which will reduce permanganate slowly, and this is why it is well to boil the solution, let it stand some time before using it, and then filter it. Manganese dioxide is usually formed when the permanganate decomposes, and the presence of this substance serves to catalyze further decomposition so that it should be removed by filtration.

STANDARDIZATION OF PERMANGANATE SOLUTION

1. Against Sodium Oxalate (Sörensen)[1]

1000 ml of 0.1 N permanganate solution = 6.700 g $Na_2C_2O_4$

Sodium oxalate suitable for standardizing solutions can be obtained from the National Bureau of Standards at Washington, D.C. This is the most reliable standard of all those that have been proposed. Dry the sample for an hour at 130°. For the standardization Fowler and Bright[2] recommend the following procedure.

Procedure. Transfer 0.3 g of sodium oxalate (dried at 105°C) to a 600-ml beaker. Add 250 ml of diluted sulfuric acid (5 + 95)[3] previously boiled for 10 to 15 minutes and then cooled to 27 ± 3°C. Stir until the oxalate has dissolved. Add 39 to 40 ml of 0.1 N potassium permanganate at a rate of 25 to 35 ml per minute while stirring slowly. Let stand until the pink color disappears (about 45 seconds). Heat to 55 to 60°C, and complete the titration by adding permanganate until a faint pink color persists for 30 seconds. Add the last 0.5 to 1 ml dropwise with particular care to allow each drop to become decolorized before the next is introduced.

[1] Z. anal. Chem., 42, 352, 512 (1903); 45, 272 (1905).

[2] J. Research Natl. Bur. Standards, 15, 493 (1935).

[3] This means 5 ml concentrated acid + 95 ml water.

Determine the excess of permanganate required to impart a pink color to the solution. This can be done by matching the color by adding permanganate to the same volume of the boiled and cooled diluted sulfuric acid at 55 to 60°C. This correction usually amounts to 0.03 to 0.05 ml.

2. Against Oxalic Acid

Owing to its water of crystallization, oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, is not so reliable a standard as the sodium salt. Its equivalent weight is ½ mole = 63.03, the same as when it acts as an acid.

It is sometimes desirable to check up the oxidimetric and alkalimetric standards; oxalic acid, potassium binoxalate, or potassium tetroxalate can serve for this purpose. The method of titrating is the same as in 1. The equivalent weights of these three substances are quite similar as reducing agents but very different as acids. Thus in a liter of aqueous solution the tabulated relationships hold.

Weight per Liter	Normality as Acid	Normality as Reducer
0.5 mole = 63 03 g $H_2C_2O_4 \cdot 2H_2O$	$1\,N$	$1\,N$
0 5 mole = 64 06 g KHC_2O_4	$0.5\,N$	$1\,N$
0.25 mole = 63 55 g $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$	$0.75\,N$	$1\,N$

3. Against Metallic Iron

It was formerly the general practice to standardize permanganate against iron wire, particularly when the standard solution was to be used for the titration of iron ores. The practice is not to be recommended because of the readiness with which the material rusts and because a low carbon content influences the results, not always in the same way. If, however, a solution of permanganate is standardized against sodium oxalate and also against iron wire, then the *apparent* iron value of the wire is known and it can be used as a standard. The method is as follows.

Weigh out 0.2 g of the wire into a 200-250-ml flask as shown in Fig. 84a. Displace the air by introducing a stream of carbon dioxide which has passed through a bottle containing water and another containing copper sulfate solution (to remove H_2S). Dissolve the wire in 55 ml of 3.6 N sulfuric acid. During the dissolving of the wire, sup-

port the flask as shown in the drawing, and with the gas-exit tube closed with a rubber stopper which is connected with a Bunsen valve.[1]
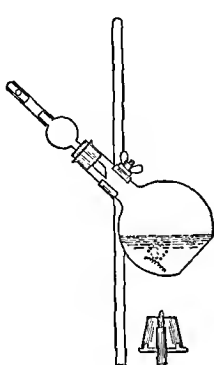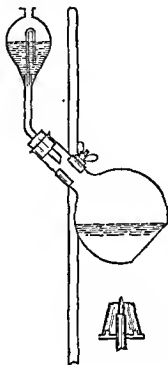
FIG. 84a. FIG. 84b.

Heat the contents of the flask by means of a low flame until the wire has entirely dissolved, then boil the solution gently for a short time. Allow to cool, remove the stopper, and titrate with permanganate.

4. Against Sodium Thiosulfate

See " Iodimetry."

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[1] A Bunsen valve consists of a short piece of rubber tubing with a cut along a few centimeters on one side, and the outer end of the tubing is closed by a glass rod. This valve prevents the entrance of air from without. A flask larger than 250-ml capacity is likely to be so thin as to break during the cooling of the iron solution. In Fig. 84a, instead of a glass rod at the end of the valve, a glass tube is used which is sealed at one end and has a hole on one side. This tube serves to prevent the collapse of the rubber tubing at the place where the slit is formed. Instead of the Bunsen valve, the Contat-Göckel valve can be used as shown in Fig. 84b. The funnel contains sodium bicarbonate which is drawn into the flask below as the solution cools, thereby filling the flask with carbon dioxide, the pressure of which stops the flow of solution into the flask.

5. Against Hydrogen Peroxide

See " Gas Analysis."

6. Against Ferrous Ammonium Sulfate

$$(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$$

Mohr proposed the use of this salt as a standard and it can be purchased in a high state of purity. The equivalent weight is 392.14 or nearly 6 times as large as that of sodium oxalate. This makes it easier to weigh out a sample accurately to four significant figures. The substance is not so reliable a standard because of the danger of losing water of crystallization and of oxidizing. Thus a sample weighed out and allowed to stand in a moist beaker for some time is likely to undergo partial oxidation. The best way to determine whether a sample is suitable is to check up the standardization values obtained with this substance and with sodium oxalate. The gravimetric determination of the iron content is likely to lead to error; usually the values for iron are found a little too high and this gives low results in the standardization.

Procedure. For the standardization of 0.1 N permanganate, weigh out samples of about 1.5 g to four significant figures. Add 10 ml of 18 N sulfuric acid, dilute to 100 ml, and at once titrate.

7. Against Arsenious Oxide, As_2O_3

Arsenious oxide can be obtained in a state of high purity and has been used a great deal in iodimetry. The reaction

$$5AsCl_3 + 2MnO_4^- + 12H_2O \rightarrow 5H_3AsO_4 + 2Mn^{++} + 15Cl^- + 9H^+$$

takes place smoothly at the beginning but a yellowish-green color soon appears as a result of the formation of some trivalent manganic salt. In a hot solution the reaction can be carried out as indicated, but it is better to add a trace of iodate or iodide as catalyzer because permanganate can be reduced by hot hydrochloric acid.

Procedure. Weigh out 0.2 to 0.25 g of pure As_2O_3 to four significant figures. Dissolve the oxide at room temperature in 10–15 ml of 6 N HCl; if the solution was boiled some $AsCl_3$ would be lost by volatilization. Dilute the solution with 50 ml of water, add 1 drop of 0.002 M KIO_3 solution, and titrate with permanganate to the first rose color. The milliequivalent of As_2O_3 is 0.01946 g.

Stability of Potassium Permanganate Solutions

A *pure* permanganate solution will keep indefinitely, provided that it is kept free from dust and reducing vapors.[1] For very accurate work, however, it is advisable to standardize the solution frequently. The addition of 10 g caustic potash per liter increases the stability of the solution.

Uses of Permanganate Solution

1. Determination of Iron

Method of Margueritte (1846)

$$1 \text{ ml of } 0.1 \ N \text{ KMnO}_4 \text{ corresponds to} \begin{cases} 0.005585 \text{ g Fe} \\ 0.007185 \text{ g FeO} \\ 0.007985 \text{ g Fe}_2O_3 \end{cases}$$

In this determination the iron is oxidized from the ferrous to the ferric condition:

$$\text{MnO}_4^- + 5\text{Fe}^{++} + 8\text{H}^+ \rightarrow \text{Mn}^{++} + 5\text{Fe}^{+++} + 4\text{H}_2\text{O}$$
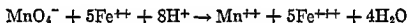
To each 100 ml of the ferrous salt solution add 5 ml of 6 N sulfuric acid, and at a volume of about 400 ml titrate in the cold by adding potassium permanganate from a buret with glass stopcock until a permanent pink color is obtained.

This determination affords very accurate results and is unquestionably one of the best methods for determining iron. It, like all other procedures for titrating iron with an oxidizing solution, depends upon the preliminary reduction of any ferric iron to the ferrous state and sulfuric acid is the only permissible acid with this procedure.

REDUCTION OF FERRIC SALTS TO FERROUS SALTS

The reduction of ferric to ferrous salts can be accomplished in a number of different ways.

1. By Hydrogen Sulfide

Saturate the solution with hydrogen sulfide and boil off the excess while introducing CO_2 into the solution which is contained in a flask.

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[1] In June, 1899, 1 ml of a KMnO₄ solution = 0.005485 g Fe; in March, 1900, 1 ml of the KMnO₄ solution = 0.005476 g Fe. See also Morse, Hopkins, and Walker, *Am. Chem. J.*, **18**, 401.

2. By Sulfur Dioxide

Nearly neutralize the solution containing the ferric salt with sodium carbonate,[1] add an excess of sulfurous acid, boil, and pass a current of carbon dioxide through it until the excess of the reagent is completely removed.[2] Test a drop of the solution with thiocyanate to make sure that the reduction is complete; cool in an atmosphere of carbon dioxide and titrate.

3. By Metals

Metallic zinc, cadmium, or aluminum can be used to reduce ferric ions to the ferrous state. This can be done by adding small pieces of the pure metal to the ferric solution in a flask like that shown in Fig. 84a on p. 540 and heating on the water bath until the ferric solution is reduced and all the excess metal dissolved or removed by rapid filtration through a funnel containing a platinum cone. In carrying out such reductions it must be remembered that titanium, which is likely to be present in small quantities of most rocks, is reduced by these metals to the trivalent condition, whereas it is not reduced by hydrogen sulfide or sulfurous acid. Instead of pure zinc, chemists often prefer to use amalgamated zinc in a so-called *Jones reductor* (Fig. 85). The amalgamated zinc does not react with dilute sulfuric acid and liberate hydrogen but does reduce ferric sulfate solutions because, as the table of oxidation potential shows (p. 532), ferric ions are much easier to reduce than hydrogen ions.

To prepare a Jones reductor, take some 20- to 30-mesh zinc, cover with dilute hydrochloric acid, and add mercuric chloride solution while stirring up the zinc, until the evolution of hydrogen ceases. In the bottom of the reductor tube place a perforated disk or some pieces of glass, on top of this a wad of glass wool, and then just a little asbestos suspension (p. 30). If this asbestos layer is too thick, the reductor is likely to run slowly, and if too thin, some zinc powder may run through and spoil an analysis. Fill the rest of the reductor tube with the well-washed, amalgamated zinc. The use of the reductor is explained below.

Determination of Iron in Iron Ore with the Jones Reductor. Weigh out 0.5-g samples to four significant figures and dissolve by heating with 20 ml of 6 N hydrochloric acid. To the resulting ferric chloride solution add 12 ml of 18 N sulfuric acid and evaporate, without boiling, until all hydrochloric acid has been removed, as shown by the lack of odor or by the formation of sulfuric acid fumes. Cool, dilute carefully with 100 ml of water, and run through the properly prepared reductor with which blanks have just been run. From the total volume of permanganate

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[1] Ferric salts are not completely reduced by sulfurous acid in the presence of considerable hydrochloric or sulfuric acid.

[2] It is not advisable to depend upon the sense of smell. Test escaping gas from the flask by passing it through dilute sulfuric acid containing a few drops of 0.1 N KMnO₄ solution. If the latter is not decolorized at the end of 2 or 3 minutes, the excess of sulfurous acid has been removed.

solution used in the analysis, **deduct** the volume required in the blank.

In making blanks and in all determinations, the procedure is as follows. Add 100 ml of normal sulfuric acid through the funnel B,
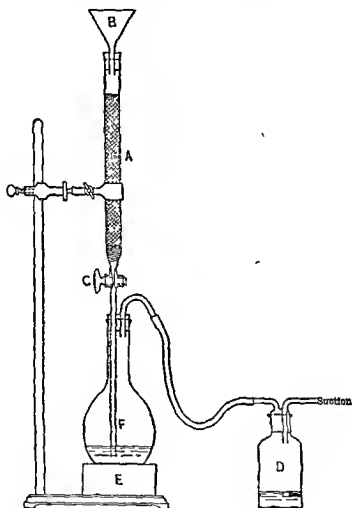
FIG. 85.

with the stopcock C open, using a little suction. When only a little of the dilute acid remains in the funnel, add the solution to be reduced or, in the case of blanks, 50 ml of $1.5 N$ sulfuric acid, and when this has nearly passed out of the funnel, follow with 250 ml of normal sulfuric acid, washing out the original beaker with this acid and adding it in small portions. Finally, pass 100 ml of water through the reductor. At no time, however, should **any air be** allowed to enter the reductor tube, which should always be kept full of water when idle. Run blanks until two successive tests require less than 0.2 ml of $0.1 N$ permanganate to give a pink color to the acid solution.

4. By Stannous Chloride

This method is especially suited for metallurgical purposes, because it can be accomplished most rapidly and hydrochloric acid is the best solvent for iron ores.

Ferric chloride in hot solution is easily reduced by stannous chloride:

$$SnCl_2 + 2FeCl_3 + 2HCl = H_2SnCl_4 + 2FeCl_2$$

The complete decolorization of the solution shows the end point of reduction. The excess of stannous chloride is afterward oxidized by means of mercuric chloride:

$$SnCl_2 + 2HgCl_2 + 2HCl = H_2SnCl_4 + Hg_2Cl_2$$

Requirements. (a) Stannous chloride solution. Dissolve 50 g of stannous chloride in 100 ml of concentrated hydrochloric acid and dilute with water to a volume of 1 l.

(b) 6 N hydrochloric acid.

(c) Mercuric chloride solution. A saturated solution of the pure commercial salt in water is used.

(d) Manganese sulfate solution. Dissolve 67 g of crystallized manganous sulfate (MnSO$_4$·4H$_2$O) in 500–600 ml of water; add 138 ml of phosphoric acid (d 1.7) and 130 ml of concentrated sulfuric acid; dilute the mixture to 1 l.

Determination of Iron in an Ore by the Zimmermann-Reinhardt Method

Procedure. Weigh out 0.25–0.3 g of the finely powdered mineral into a small beaker, add 20 ml of 6 N hydrochloric acid, cover the beaker with a watch glass, and heat, just below the boiling temperature, until the residue is apparently free from reddish brown mineral. Remove the flame, and add the stannous chloride solution, *drop by drop*, until the iron solution just becomes colorless, avoiding an excess. Cool to at least room temperature and add quickly 10 ml of mercuric chloride solution, whereby a slight silky precipitate of Hg$_2$Cl$_2$ is formed.[1] After 5 minutes, dilute the solution to about 400 ml, add 20–25 ml of the manganese sulfate solution, and titrate the cold mixture (very slowly) with potassium permanganate until a pink color permanent for 15 seconds is obtained. Toward the last take care not to add a drop of permanganate until the color of the preceding drop has disappeared.

TITRATION OF FERROUS SALTS IN HYDROCHLORIC ACID SOLUTION

The titration of iron in hydrochloric acid solution gives high results unless particular precautions are taken. If dilute permanganate solution is allowed to run

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[1] If the precipitate produced by mercuric chloride is at all grayish in color, the solution must be thrown away; too large an excess of stannous chloride was used. Moreover, the end point with permanganate is difficult to see if the solution contains much precipitate.

into a cold dilute solution of ferrous chloride containing hydrochloric acid, the permanganate is decolorized and the iron is oxidized, but there is noticeable evolution of chlorine.[1] More permanganate is used than is necessary to oxidize the ferrous salt to the ferric condition.

·If, however, permanganate is run into cold, dilute hydrochloric acid, in the absence of ferrous salt, there is no evolution of chlorine. Furthermore, the presence of a ferric salt does not cause evolution of chlorine. The chlorine, therefore, is not a result of the direct action of the permanganate upon the hydrochloric acid, but is probably due to the oxidation of the ferrous ion to an unstable state of oxidation corresponding to a perchloride, a peroxide, ferric acid, or perferric acid.

When permanganate is run into a dilute hydrochloric acid solution containing ferrous chloride and considerable manganous salt, the ferrous iron is oxidized quantitatively to ferric iron and there is no evolution of chlorine. This was shown by Kessler[2] in 1863 and by Zimmermann[3] in 1881. It has since been confirmed by many other chemists.[4]

This can be explained as follows: Permanganate ions react with manganous ions to form, as Volhard[5] proved, quadrivalent manganese. In this state of oxidation, manganese is unstable in acid solution, but it is reduced more readily by ferrous ions than by chloride ions.

Zimmermann[6] suspected, and Manchot's[7] experiments confirm this view, that iron like manganese has a tendency to form unstable compounds as primary oxidation products. If such a compound is formed in the presence of manganous ions, the iron will give up its excess charge to manganous rather than to chloride ions, provided that sufficient manganous ions are present.

According to Manchot there is a tendency in all oxidations to form an unstable compound as the primary oxidation product. When hydrogen burns in air, a little hydrogen peroxide is formed; when sodium burns, sodium peroxide results. In most cases, these primary products are unstable and cannot be isolated because of the readiness with which they are reduced to a more stable condition. When an acceptor[8] is present it will take up the excess charge which is lost when the primary product is reduced; in aqueous solutions in the absence of any other acceptor, free oxygen is evolved.

According to the method of oxidation, iron tends to form different primary states of oxidation. In the direct oxidation of iron by oxygen, the primary oxide appears to be FeO_3; in the oxidation by means of permanganate, chromic acid, or hydrogen peroxide, the primary oxidation product appears to contain iron with a valence of 5, whereas iron with a valence of 6 is probably formed if hypochlorous acid is the oxidizer.

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[1] Löwenthal and Lenssen, Z. anal. Chem., 1863, 329.

[2] Pogg. Ann., 118, 779, and 119, 225.

[3] Ber., 14, 779, and Ann. Chem. Pharm., 213, 302.

[4] For example, J. A. Friend, J. Chem. Soc., 95, 1228 (1909). C. C. Jones and J. H. Jeffery, Analyst, 34, 306 (1909).

[5] Ann. Chem. Pharm., 198, 337.

[6] Ber., 11, 779, and Ann. Chem. Pharm., 213, 302.

[7] Ann. Chem. Pharm., 325, 105 (1902).

[8] An acceptor is a substance which is not oxidized by oxygen alone, but can be oxidized by the aid of some other substance present called an 'auto-oxidator.' A substance which tends to be peroxidized may play the part of an acceptor. Cf. Engler, Ber., 33, 1097 (1900).

According to Manchot, potassium permanganate first causes the formation of quinquevalent iron. If sufficient manganese ions are present, these play the part of acceptor, but otherwise, in hydrochloric acid solution, some chlorine is formed:

$$3MnO_4^- + 5Fe^{++} + 24H^+ \rightarrow 3Mn^{+++} + 5Fe^{+++} + 12H_2O$$

$$\overset{+++}{Fe} + \overset{++}{Mn} \rightarrow \overset{++}{Mn} + Fe^{+++}$$

$$\overset{++}{Mn} + 2Fe^{++} \rightarrow \overset{'}{Mn} + 2Fe^{+++}$$

$$\overset{+++}{Fe} + 2Cl^- \rightarrow Cl_2 + Fe^{+++}$$
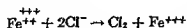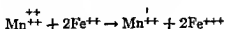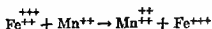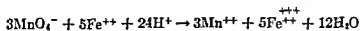
The action of the manganous sulfate is partly to regulate the reaction between ferrous and permanganate ions, for, according to Volhard, the manganous ions tend to react with permanganate, thus slowing down the reaction between permanganate and ferrous ions. The quadrivalent manganese formed by the action of permanganate on manganous ions at once reacts with ferrous ions; the manganous ions also act as acceptor toward any iron oxidized above the trivalent state. In both cases it is essential that manganese peroxide does not react with hydrochloric acid very rapidly, and it is necessary, too, that the amount of manganous salt shall greatly exceed the amount of iron present

Although it is possible, then, to titrate iron in hydrochloric acid solutions in the presence of manganous sulfate, the method possesses the disadvantage that the end point cannot be seen so distinctly as when no chloride is present, since ferric chloride forms a much more yellow solution than does ferric sulfate. This difficulty is overcome by the addition of phosphoric acid as suggested by C. Reinhardt. The titration in hydrochloric acid in the presence of manganese sulfate and phosphoric acid is called the Zimmermann-Reinhardt method (cf. p. 545).

Determination of Metallic Iron in the Presence of Iron Oxide

This method is useful for testing *ferrum reductum*, which is obtained by the reduction of Fe_2O_3 in a stream of hydrogen. Usually the reduction is not complete and the preparation contains, besides the metallic iron, some oxide, usually assumed to be Fe_3O_4. The value of the preparation depends upon the free iron content.

α. Method of Wilner-Merck [2]

Principle. The method is based upon the fact that a neutral solution of mercuric chloride dissolves iron according to the equation

$$Fe + HgCl_2 = Hg + FeCl_2$$
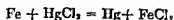
while the Fe_3O_4 is not attacked. The solution of ferrous chloride is titrated with permanganate solution.

[1] *Farm. Tidskrift*, 1880, 225.

[2] *Z. anal. Chem.*, 41, 710 (1902).

Procedure. Place about 0.5 g of *ferrum reductum* powder[1] in a 100-ml graduated flask, from which the air has been replaced by CO_2; add 3 g of solid mercuric chloride and 50 ml of water. Heat the contents of the flask to boiling, by means of a small flame, and boil gently for a minute. Then fill the flask to the mark with boiled water. Cool to 20° and again carefully bring to the mark. Shake well, and allow to stand in the stoppered flask until the precipitate has settled. Pour the liquid through a dry filter, reject the first 15 ml, and catch 20 ml of filtrate in a flask filled with carbon dioxide. To this add 20 ml of 7 N sulfuric acid and 10 ml of manganese sulfate solution,[2] dilute to 200 ml, and titrate with 0.1 N permanganate solution.

β. The Ferric Chloride Method[3]

Principle. A neutral solution of ferric chloride dissolves metallic iron with the formation of ferrous chloride:

$$Fe + 2FeCl_3 = 3FeCl_2$$

If the ferrous chloride formed is titrated with permanganate solution, one-third of the iron thus found corresponds to the weight of metallic iron present in the sample.

Proceed in exactly the same manner as in (α) but use 50 ml of ferric chloride solution, obtained by dissolving 2.5 g of anhydrous ferric chloride in cold water, instead of the 3 g of mercuric chloride. Stopper the flask and shake 15 minutes in an atmosphere of CO_2 before diluting to the mark. The ferric chloride should give a clear solution in cold water and be perfectly free from ferrous salt.

2. Determination of Manganese in Steel

Manganese exists in ordinary steels as a solid solution with iron. Small quantities of manganese may be present as manganous sulfide or silicate, forming a part of the slag that is unintentionally left in the steel; breaks in the metal often start from such inclusions. Manganese, in the form of ferromanganese or "spiegeleisen," is introduced into molten steel for the purpose of deoxidizing and desulfurizing the metal and to prevent "red shortness" or brittleness during the forging heats. Some excess always appears in the finished steel, which ordinarily contains 0.2 to about 1.0 per cent. Manganese tends to increase the hardness and decreases somewhat the ductility of ordinary steels.

In metals containing more than 1 per cent of manganese, the hardness and brittleness increase rapidly, reaching maximums between 5 and 6 per cent, when it is prac-

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[1] A coarse powder is not decomposed quantitatively.

[2] See p. 545.

[3] A. Christensen, *Z. anal. Chem.*, 44, 535 (1905); see, also, E. Schmidt, *Chem. Ztg.*, 21, 700 (1897); A. Marquardt, *Chem. Ztg.*, 25, 743 (1901); F. Förster and V. Herold, *Z. Elektrochem.*, 16, 461 (1910).

tically impossible to machine the metal with any tool. Beyond 7 per cent of manganese causes progressive increase in the ductility, and steels containing 13 per cent manganese are very strong, tough, and ductile. The addition of manganese to steel lowers the transformation temperatures (see " Carbon ") and makes the transformations take place in a sluggish manner. Sometimes the A_{r1} point (see p. 342) falls below the ordinary room temperature and self-hardening steels result.

Samples of iron or steel are usually dissolved in hot dilute nitric acid when manganese is to be determined. If tungsten is present, sulfuric acid is commonly used followed by nitric and sometimes phosphoric acid.

Usually it is not necessary to get rid of the iron before attempting to determine manganese because reactions typical of manganese can be made to take place in the presence of considerable quantities of ferric salt.

A fair separation of manganese from iron can be accomplished with ammonia and ammonium chloride, but when much iron and little manganese are present this method is rarely used; the precipitate of ferric hydroxide is very bulky and hard to handle, and the separation is never satisfactory with a single precipitation. The basic acetate separation, which depends upon the precipitation of basic ferric acetate, ferric phosphate, etc., by boiling the faintly acid solution with considerable sodium acetate, is better but also very tedious. More satisfactory is the treatment with an emulsion of zinc oxide and water. This serves to precipitate hydroxides which are more insoluble than zinc oxide. When this treatment is carried through it is customary to make up the solution and precipitate to a definite volume, mix well, and take a fraction (aliquot) of the filtered solution for the subsequent analysis. A slight error is introduced by the volume occupied by the precipitate, but the actual weight of the precipitate from 3 g of steel in 500 g of solution is relatively small, and the bulky ferric hydroxide precipitate tends to adsorb enough manganese to compensate for the fact that the actual volume of solution is somewhat less than 500 ml.

Two other methods of separating ferric and manganous . . .

. . .

acid solution (d 1.10) is shaken with a larger volume of ether, nearly all the ferric chloride, considerable hydrochloric acid, but no manganous chloride will pass into the ether layer. This is the Rothe ether separation, which has been much used in analytical chemistry. (2) If a dilute hydrochloric acid solution of ferric and manganous chlorides is treated with cupferron — the ammonium salt of phenylnitrosohydroxylamine, $C_6H_5(NO)NONH_4$ — ferric ions are precipitated as the salt of cupferron; in 3 cupferron molecules the NH_4 groups are replaced by Fe.

Practically all methods used for determining manganese in steel, or other ferrous alloys, are based upon the oxidation of bivalent manganous ions to some higher valency. In one method (Volhard's) the quantity of oxidizing agent ($KMnO_4$) required to accomplish the oxidation is measured, but in most methods the oxidized manganese is treated with a carefully measured quantity of reducing agent and the excess determined by titration with permanganate. Sometimes the analysis is finished by comparing the color of the permanganate produced by suitable oxidation with that corresponding to known quantities of permanganate. In this book four methods of determining manganese in steel will be described.

Volhard Method[1]

$$1000 \text{ ml } N \text{ KMnO}_4 = \frac{3\text{Mn}}{10} = 16.48 \text{ g Mn}$$

If an almost boiling, nearly neutral solution of manganese sulfate is slowly treated with a solution of potassium permanganate, each drop will cause the formation of manganous acid (H_2MnO_3). Under ideal conditions the reaction takes place as follows:

$$2\text{MnO}_4^- + 3\text{Mn}^{++} + 7\text{H}_2\text{O} \rightarrow 5\text{H}_2\text{MnO}_3 + 4\text{H}^+$$
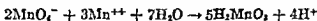
According to this equation, 2KMnO_4 (10 equivalents) react with 3Mn^{++} (cf. p. 537).

A. Guyard, who first determined manganese by this method, assumed that the oxidation took place according to the above equation.

In reality, however, instead of pure manganous acid being precipitated, different acid manganites of varying composition are formed; for example:

$$4\text{KMnO}_4 + 11\text{MnSO}_4 + 14\text{H}_2\text{O} = 4\text{KHSO}_4 + 7\text{H}_2\text{SO}_4 + 5\text{Mn}(\text{HMnO}_3)_3$$
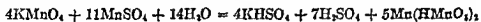
Volhard has shown that if calcium, barium, or, better still, zinc salts, are present, manganites of these metals are precipitated. The precipitate, although varying in composition, then contains all *the manganese in the quadrivalent form.*

Weigh out, to three significant figures, three separate portions of 2 g of steel into 300-ml porcelain casseroles. Cover the dishes with watch glasses, and dissolve each sample by the gradual addition of 25 ml of 6 N nitric acid. When the sample has dissolved, raise the cover glass, evaporate to dryness, and ignite carefully to decompose nitrates. Cool and digest the residue with 20 ml of concentrated hydrochloric acid.

If a dark residue remains undissolved, evaporate the solution to dryness again, dehydrate silica by heating an hour at 125°, warm with 10 ml of concentrated hydrochloric acid, dilute, filter, and wash the residue thoroughly, first with a little hot 2 N hydrochloric acid, then with cold water, and finally with hot water. If there is no dark-colored residue containing graphite, this treatment is unnecessary. A carbonaceous residue is always more or less oxidizable and must be removed.

Evaporate the hydrochloric acid to dryness. Moisten the residue with 10 ml of 6 N hydrochloric acid, warm, and evaporate to a small volume but not to dryness. Transfer to a 500-ml measuring flask, first filtering if there is much residue, and dilute with cold water to about 200 ml. Add 6 N sodium carbonate solution in small portions until the ferric chloride solution has a deep red color and then small quantities of a suspension of zinc oxide in water, shaking after each addition of oxide and continuing until a point is reached where the liquid suddenly coagulates forming a heavy precipitate of ferric hydroxide. Fill the flask with

[1] *Ann. Chem. Pharm.,* **198,** 318 (1879). Cf. W. Fischer, *Z. anal. Chem.,* **48,** 751 (1909); Cahin and Little, *Analyst,* **36,** 52 (1911). The method was really proposed first by Morawski and Stingl, *Chem. News,* **38,** 297 (1878).

water up to the mark, mix thoroughly by pouring back and forth into a beaker several times, allow the precipitate to settle, and filter through a dry 18–20 cm filter. Reject the first 5 ml of filtrate and collect the next 250 ml in a measuring flask. Transfer the solution to a 500-ml flat-bottomed flask, add 5 ml of 6 N acetic acid, and titrate until the hot solution (80–90°) appears pink above the brown precipitate, best viewed in the neck of the flask against a light background. Add the $KMnO_4$ in milliliter portions to the first sample until the end point is overstepped. To the other samples, add nearly all the requisite $KMnO_4$ at once.

Bismuthate Method[1]

1000 ml N $KMnO_4$ = 10.99 g Mn

This method originated with Schneider,[2] who used bismuth tetroxide as the oxidizing agent; but as the oxide is difficult to prepare free from chlorides, and traces of chlorido interfere with the end point of the titration, it was abandoned by Reddrop and Ramage,[3] who proposed the use of sodium bismuthate, $NaBiO_3$. The product sold under this name is of more or less indefinite composition.

The determination is based on the fact that a manganous salt in the presence of nitric acid is oxidized to permanganic acid by sodium bismuthate.

$$2Mn^{++} + 5NaBiO_3 + 14H^+ \rightarrow 2MnO_4^- + 5Bi^{+++} + 5Na^+ + 7H_2O$$

The permanganic acid formed is very stable in a cold solution containing 20–40 per cent of nitric acid. In hot solutions the excess of bismuthate is rapidly decomposed and then the permanganic acid breaks down; as soon as a small amount of manganous salt is formed it reacts with the permanganic acid and manganese dioxide precipitates.

In the cold, however, the excess of the bismuth salt can be filtered off, an excess of ferrous sulfate added to the clear filtrate, and the excess determined by titrating with permanganate. The end point is sharp, and the method is extremely accurate except in the presence of cobalt.[4]

The following conditions are recommended by Blum. To the cold manganous solution containing 20–40 per cent nitric acid (free from nitrous acid) in a volume of 50–150 ml, add a slight excess of bismuthate (usually 0.5–1.0 g), agitate thoroughly for about ½ minute, wash down the sides of the flask with 3 per cent nitric acid,[5] filter through asbestos, wash with 100 ml of 3 per cent nitric acid, add a slight excess of ferrous sulfate solution (p. 576), and titrate at once with permanganate.

[1] A. A. Blair, *J. Am. Chem. Soc.*, **26**, 793. W. Blum, Reprint No. 186 from *Bull. Bur. Standards*, **8** (1912).

[2] *Dinglers Polytech. J.*, **269**, 224.

[3] *Trans. Chem. Soc.*, 1895, 268.

[4] G. E. F. Lundell, *J. Am. Chem. Soc.*, **45**, 2600 (1923).

[5] One milliliter of nitric acid, d 1.42, contains nearly 1 g of HNO_3. The solution of

Procedure. Dissolve 1 g of sample in 50 ml of 4 N nitric acid and boil the solution to expel oxides of nitrogen. Remove from the heat, add about 0.5 g of sodium bismuthate, and boil 2 to 3 minutes. If more than 0.1 per cent manganese is present, a precipitate of manganese dioxide usually appears or, if the manganese content is low, a pink color is produced. If neither a pink color nor a precipitate is produced, add more bismuthate and heat again. Clear the solution by adding a few drops of sulfurous acid, boil 2 to 3 minutes, and cool to 15°. Add 0.5 to 1 g more of bismuthate (enough to leave a *small* excess undissolved) to the *cold* solution, agitate, and allow to stand for 1 minute. Then add 50 ml of 3 per cent nitric acid (3 ml of concentrated HNO_3 + 97 ml of water), and filter through asbestos. A suitable filter can be made by tamping down some glass wool in a funnel and pouring some asbestos fibers suspended in water upon it. If a Gooch crucible is used for filtering, take care that none of the filtrate comes in contact with the rubber that holds the crucible in the filter bottle. A glass filtering crucible can be used. Wash the excess bismuthate with 3 per cent nitric acid until the last runnings are colorless (50 to 100 ml of acid should be used). Add a measured volume of standard ferrous sulfate solution (see p. 576; usually a 25-ml pipetful is sufficient), and titrate the excess with permanganate.[1]

The ratio of permanganate to ferrous sulfate solution must be determined daily. Though not strictly necessary, the determination of this ratio by means of a blank affords a convenient means of testing the efficacy of the filter.

The manganese content of the steel can be computed as follows:

Let s = *weight of the sample.*
A = volume of $KMnO_4$ which is equivalent to the $FeSO_4$ used.
n = volume of $KMnO_4$ used to titrate the excess $FeSO_4$.
N = the normality of the $KMnO_4$ solution.

$$\frac{(A-n)N \times 0.01099 \times 100}{s} = \text{per cent Mn}$$

It was originally assumed that the bismuthate method was not well suited for determining large quantities of manganese, but Cunningham and Coltman[2] have shown how the method can be applied to materials rich in manganese.

A modification of the bismuthate method which is useful for rapid work depends upon reducing the permanganate formed with a sodium arsenite solution. (See Persulfate Method, which follows.)

[1] H. F. V. Little, *Analyst,* 37, 554 (1912), found that it was advisable to filter into a known volume of standardized ferrous solution when the manganese content was high.

[2] *Ind. Eng. Chem.,* 16, 58–63 (1924). Cf. Little, *loc. cit.*

Interfering Substances. Cobalt, cerium, and nitrous, hydrochloric, and hydrofluoric acids, large quantities of phosphoric acid, and, to a lesser degree, chromium and vanadium interfere with the bismuthate method. The carbonaceous residue obtained when cast iron is treated with nitric acid also interferes and must be filtered off. Interference of cobalt cannot be overcome as cobalt is oxidized to the cobaltic state and is subsequently reduced by the added ferrous sulfate. When cobalt is ⋯ ⋯ ⋯ ⋯ ⋯ ⋯ ⋯ ⋯ ⋯ ⋯ Cerium is seldom present, permanganate, formed by te, which does not reduce quadrivalent ceric ions. The error caused by chromium is not serious unless more than 1 per cent is present. Interference by large quantities of chromium can be o ⋯ ⋯ ⋯ ⋯ ⋯ the chromium in either of the following two ways: (a) Digest 1 ⋯ ⋯ ⋯ ⋯ Dilute the resulting solution to 100 a ⋯ ⋯ while stirring, sufficient 8 per cent NaHCO$_3$ solution to give a permanent precipitate and 4 ml more. Boil 1 minute, filter off the Cr(OH)$_3$, and some Fe(OH)$_3$ formed by atmospheric oxidation, and wash 5 times with hot water. Pay no attention to a cloudy filtrate caused by the gradual oxidation of more of the ferrous iron. Use the filtrate for the manganese determination. (b) Heat gently 1 g of sample in a 500-ml flask with a mixture of 1 part 2.5 N HCl and 4 parts of 72 per cent HClO$_4$. When the sample has dissolved, heat on the hot plate with gradually increasing temperature and finally fume 5 to 10 minutes until all the chromium is oxidized to CrO$_3$. Then, to volatilize the chromium as CrO$_2$Cl$_2$, add 1 to 4 g of NaCl in small portions until there are no more brown fumes of chromyl chloride. After the last addition of NaCl, boil the solution for 1 minute to remove HCl, add HNO$_3$, H$_2$SO$_4$, and H$_3$PO$_4$, and determine the manganese by the persulfate method.

Persulfate Method[1]

In a hot solution of a manganous salt containing silver nitrate as catalyst, ammonium persulfate causes the formation of permanganic acid.

$$2Mn^{++} + 5S_2O_8^{--} + (Ag^+) + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{--} + (Ag^+) + 16H^+$$
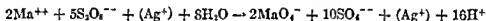
Without the silver salt, manganous acid, H$_2$MnO$_3$, is precipitated. In the routine analysis of steel it is customary to discharge the permanganate color by adding standard sodium arsenite. Under the conditions that usually prevail, the arsenic is completely oxidized to the quinquevalent condition; the manganese of the permanganate is not reduced to colorless manganous salt but to a solution which contains manganese partly trivalent and partly quinquevalent. The solution has greenish yellow tint at the end point when more than a few milligrams of manganese are present. The arsenite solution, therefore, must be standardized in exactly the same way it is used in the analysis against permanganate solution or by means of a Bureau of Standards steel. If, however, the titration is made with the following sodium arsenite and nitrite solution, the HMnO$_4$ is reduced completely to the bivalent state.[2] Dissolve 1.3 g of pure As$_2$O$_3$ in 25 ml of 4 N NaOH, dilute to 200 ml, make

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[1] Walters, *Proc. Eng. Soc. Western Pa.*, 17, 257 (1901); *Chem. News*, 84, 239. H. P. Smith, *Chem. News*, 90, 237 (1904). Rubricus, *Chem. Ztg. Repert.*, 1905, 217. F. Kunze, *Chem. Ztg.*, 29, 1017 (1905). H. Marshall, *Z. anal. Chem.*, 43, 418, 655 (1904).

[2] Sandell, Kolthoff, and Lingane, *Ind. Eng. Chem., Anal. Ed.*, 7, 256 (1935).

acid with dilute H_2SO_4, and then make neutral to litmus by adding $NaHCO_3$. Add 0.85 g of $NaNO_2$ and dilute to 1 l.

Dissolving Solution. Mix together 5 ml of 0.1 N $AgNO_3$, 40 ml of water, 2 ml of concentrated H_2SO_4, and 15 ml of concentrated HNO_3.

Titrating Solution. Dissolve exactly 0.337 g of pure As_2O_3 and about 1.1 g of Na_2CO_3 in about 60 ml of hot water. When the solids have dissolved completely, transfer to a liter measuring flask and make up to exactly 1 l. One milliliter = 0.1 mg Mn. Test the strength of the solution by taking a measured volume of 0.1 N $KMnO_4$ (2.00 ml is suitable), reducing it with a little H_2SO_3, and then proceeding exactly as in the analysis of steel, using the same quantities of reagents.

Procedure. Weigh out portions of exactly 0.100 g (within 1 mg) into 250-ml Erlenmeyer flasks, and heat each portion with 15 ml of the dissolving solution until all the steel has dissolved and the red nitrous fumes have been expelled. Remove from the hot plate; add 100 ml of hot water and 10 ml of 10 per cent $(NH_4)_2S_2O_8$ solution. Heat to boiling, and maintain this temperature for 30 seconds. Remove from the hot plate and cool under running water to about 15°. (If necessary use ice-water.) Titrate the cold solution until the permanganate color is discharged. Pay no attention to a return of the color on standing. (This can be prevented by adding to the cold solution just enough dilute NaCl to precipitate the Ag^+ as AgCl. In the absence of the Ag^+, Mn^{++} is not oxidized in the cold.)

The persulfate, in the presence of silver cations, slowly oxidizes the manganous ions to permanganate, but this reaction is so slow in the cold that there is no serious error if the titration takes place fairly quickly. If the cold solution is treated with just sufficient NaCl solution to precipitate the silver before the titration, the end point lasts much better; but if the solution is hot when the chloride is added, some permanganate will be reduced. The above very rapid method has never been regarded as suitable for umpire analysis, but students usually obtain excellent results agreeing within 0.02 per cent, or less, of the correct values. If considerable manganese is present the solution is yellow or green at the end point, but the practiced eye can easily tell when all the permanganate color is gone.

Modified Williams Method

$$1000 \text{ ml of } N \text{ } KMnO_4 = \frac{Mn}{2} = 27.47 \text{ g Mn}$$

The Williams method depends, in the first place, upon the precipitation of all the manganese as MnO_2 by boiling the manganous solution with concentrated nitric acid and potassium chlorate. The reaction has also been used in qualitative analysis.

$$Mn(NO_3)_2 + 2KClO_3 + H_2O \rightarrow MnO_2 \cdot H_2O + 2KNO_3 + 2ClO_2 \uparrow$$
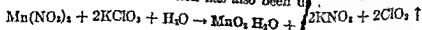
The precipitate is dissolved in acid and a known quantity of reducing agent, and the

excess of the latter is measured by titration with standard potassium permanganate solution. A standard solution of acid ferrous sulfate or ferrous ammonium sulfate (p. 576) is commonly used as the reducing agent, and since such a solution oxidizes slowly on standing in the air it is necessary to determine its strength at least once every day that it is being used.

Julian[1] used H_2O_2 as the reducing agent and did not bother to filter off the precipitate, but it is unquestionably *better to do so because the presence of a little nitrous acid in the solution is likely to cause error in the final titration.*

Procedure. Take 2 to 3 g of steel (weighed to the nearest centigram) in a 500-ml Erlenmeyer flask and dissolve it in 60 ml of 6 N HNO_3. When the steel has dissolved, evaporate the solution to sirupy consistency (about 10 ml); add 50 ml of concentrated nitric acid and 3 g of potassium chlorate crystals. Boil the solution on the hot plate for 15 minutes. Then remove the flask from the hot plate, as otherwise the ClO_2 which *is liberated on adding chlorate may explode*; add 15 ml more of concentrated nitric acid and another 3 g of potassium chlorate. Boil for another 15 minutes. Cool quickly by placing the flask in cold water and rotating the contents. Prepare an asbestos filter by pressing down a little glass wool in a funnel and pouring on it a little asbestos suspension such as is used for Gooch crucibles. Filter through the asbestos, and wash the MnO_2 precipitate with three 10-ml portions of cold water. Transfer the asbestos pad and precipitate back to the original flask. As solvent, prepare a mixture of 900 ml water, 43 ml of 3 per cent hydrogen peroxide, 25 ml of phosphoric acid, d 1.70, and 25 ml of concentrated sulfuric acid; keep the solution in a glass-stoppered bottle. Of this well-mixed solution take out 25-ml portions by means of a pipet. Usually one portion of the solution is sufficient to dissolve the MnO_2 precipitate and leave an excess of H_2O_2. At the same time, take two separate portions of the solution for direct titration with permanganate. In every case, dilute with water to about 200 ml and titrate with standard potassium permanganate. In using the pipet make sure that it has been cleaned recently with cleaning solution so that it will drain well and that it has been rinsed out with three small portions of the solution which is to be measured. Make sure that the pipet is filled from the bottom up to the mark on the stem, and, after allowing the contents to drain out, touch the tip of the pipet to the side of the beaker just above the solution. When used in this way pipets are more accurate than the ordinary buret.

The reactions that take place with the hydrogen peroxide are these:

$$H_2O_2 + MnO_2 + 2H^+ \rightarrow Mn^{++} + 2H_2O + O_2 \uparrow$$
$$5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{++} + 8H_2O + 5O_2 \uparrow$$
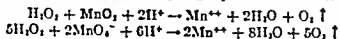
[1] *J. Am Chem. Soc.*, 15, 113 (1893); cf. *J. Anal. Chem.*, 2, 249 (1888).

If, in the analysis of s g of steel, 25 ml of H_2O_2 was used which was equivalent, as found by direct titration, to A ml of $KMnO_4$ and the excess H_2O_2 reacted with n ml of $KMnO_4$ which was N-normal, then

$$\frac{(A - n)N \times 0.02747}{s} \times 100 = \text{per cent Mn}$$

3. Determination of Uranium

Method of Belohoubek,[1] Zimmermann,[2] Hillebrand[3]

$$1000 \text{ ml } N \text{ KMnO}_4 = \frac{U}{2} = 119.0 \text{ g U}$$

This method is especially suited for testing the purity of a precipitate of U_3O_8 obtained in the analysis of uranium minerals. It is based upon the fact that when U_3O_8 is heated in a closed tube with dilute sulfuric acid at 150–175° it is readily decomposed according to the equation

$$U_3O_8 + 4H_2SO_4 = 2UO_2SO_4 + U(SO_4)_2 + 4H_2O$$

forming uranyl and uranous sulfates. The latter compound is oxidized to the former by means of potassium permanganate:

$$2KMnO_4 + 5U(SO_4)_2 + 2H_2O = 2KHSO_4 + 2MnSO_4 + H_2SO_4 + 5UO_2SO_4$$

If it is desired to express the results in terms of the original U_3O_8, of which two-thirds is not oxidized by the permanganate, then 1 ml N KMnO$_4 = \frac{U_3O_8}{2000} = 0.4211$ g U_3O_8.

Procedure. Place 1 g of U_3O_8 in a tube closed at one end, add 10–15 ml of 5 N sulfuric acid, and make the open end of the tube narrower by heating in a blast lamp and drawing it out somewhat. Remove the air in the tube by inserting a long capillary so that it reaches to the bottom of the tube containing the substance and conducting a current of carbon dioxide through it; finally seal the larger tube without removing the capillary. Heat the tube in a " bomb furnace " at 150–175° until everything has dissolved to a clear green liquid. After cooling, open the tube by making a scratch with a file and touching it with a hot glass rod. Pour the contents into a large porcelain dish, dilute with distilled water to 500–700 ml, and titrate with 0.1 N KMnO$_4$ solution until a permanent pink color is obtained.

Remark. In quantitative analysis uranium is often precipitated as ammonium uranate by ammonium hydroxide (see p. 166), and the uranate dissolves in acids forming uranyl, UO_2^{++} salts. It is possible to reduce the 6-valent uranium of the uranyl salt to 4-valent uranous salt, and uranium, like iron, titanium, and molyb-

[1] *J. prakt. Chem.*, 99, 231.
[2] *Ann. Chem. Pharm.*, 232, 285.
[3] *U. S. Geol. Survey Bull.* 78.

denum, can be determined volumetrically by reducing in a Jones reductor and titrating with $KMnO_4$, $K_2Cr_2O_7$, or $Ce(SO_4)_2$. The reduction always goes a little too far but is never completed to the trivalent state and rarely proceeds to exactly the same point in duplicate determinations. However, by bubbling air through the solution, trivalent uranium is oxidized so that all the uranium is obtained in the quadrivalent state and can be titrated to the 6-valent condition. The bubbling with air also oxidizes trivalent titanium. Quadrivalent uranium is fairly stable in cool, dilute sulfuric acid. The volumetric determination of uranium is often used for determining the uranium in a precipitate of sodium-zinc-uranyl acetate, or similar compound, and thus serves for the indirect determination of *sodium* (p. 278).

Procedure. Prepare a solution containing not more than 0.10 g uranium in 100 ml of 2 N H_2SO_4. No other substance reducible by zinc should be present, especially nitric acid. Add enough permanganate to impart a distinct, permanent pink color, cool to 20–25°, and pass through a Jones reductor (p. 544) at the rate of 50 to 100 ml a minute. Prepare the reductor for use and test the blank as described on p. 544. Wash out the reductor, after the uranyl solution has passed through it, with dilute sulfuric acid and water as in determining iron or phosphorus. Place a long glass tube in the solution and bubble air through it for 5 minutes to oxidize any trivalent uranium or trivalent titanium to the quadrivalent state; the solution will assume a clear green tint. Wash off the inside and outside of the tube and titrate with 0.1 N $KMnO_4$ of which 1 ml = 0.01190 g U.

If the procedure is used for determining *sodium*, dissolve the triple acetate precipitate (p. 278) in 50–75 ml of 2 N sulfuric acid, poured slowly over the precipitate in small portions under gentle suction. Wash out the crucible and funnel with water and add sufficient 6 N sulfuric acid to make the solution approximately 2 N.

If the titration is made with $K_2Cr_2O_7$ or $Ce(SO_4)_2$, proceed as above described up to and including the bubbling of air through the reduced solution. Then add 40 ml of 2 per cent $FeCl_3$ solution, 15 ml of 85 per cent H_3PO_4, and 6–8 drops of diphenylamine sulfonate indicator (p. 577). Titrate immediately with 0.1 N $K_2Cr_2O_7$ or $Ce(SO_4)_2$. Run a blank on all the reagents, carrying out the Jones reductor treatment, and, after bubbling air through the acid solution, add the same quantity of $FeCl_3$, H_3PO_4 and indicator.

The titration reaction is:

$$5U^{++++} + 2MnO_4^- + 2H_2O \rightarrow 5UO_2^{++} + 2Mn^{++} + 4H^+$$
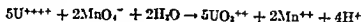
4. Determination of Oxalic Acid

$$1000 \text{ ml } N \text{ } KMnO_4 = \frac{H_2C_2O_4 \cdot 2H_2O}{2} = 63.03 \text{ g } H_2C_2O_4 \cdot 2H_2O$$

The procedure is exactly the same as was described under the standardization of permanganate by means of sodium oxalate (p. 538).

5. Determination of Calcium

$$1000 \text{ ml } N \text{ KMnO}_4 = \frac{\text{Ca}}{2} = 20.04 \text{ g Ca}$$

Precipitate the calcium as described on p. 244 in the form of its oxalate, filter, and wash with hot water. Transfer the moist precipitate to a beaker by means of a stream of water from the wash bottle, and dissolve the precipitate remaining on the filter, allowing hot $2 N$ sulfuric acid to pass through it several times. To the turbid solution in the beaker, add 20 ml of $18 N$ sulfuric acid, dilute with hot water to a volume of 300–400 ml, and titrate the oxalic acid with $0.1 N$ KMnO$_4$ solution.

6. Determination of PbO$_2$ in Minium [Red Lead, Pb$_3$O$_4$]

Method of Lux[1]

$$1000 \text{ ml } N \text{ KMnO}_4 = \frac{\text{PbO}_2}{2} = 119.6 \text{ g PbO}_2 = 342.8 \text{ g Pb}_3\text{O}_4$$

Principle. If lead peroxide (PbO$_2$) is treated with oxalic acid or sodium oxalate in acid solution, the oxalate ion is oxidized according to the following equation:

$$\text{PbO}_2 + \text{C}_2\text{O}_4^{--} + 4\text{H}^+ \rightarrow \text{Pb}^{++} + 2\text{CO}_2 + 2\text{H}_2\text{O}$$
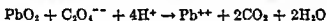
If the decomposition takes place with a measured amount of titrated oxalic acid solution and the excess of the latter is titrated by means of potassium permanganate solution, the difference shows the amount of oxalic acid necessary to effect the reduction of the lead peroxide.

Procedure. Weigh out about 0.25 g of minium (red lead) into a porcelain dish and heat with 20–30 ml of $2 N$ nitric acid. The original oxide is thereby changed into soluble lead nitrate and brown, insoluble H$_2$PbO$_3$:

$$\text{Pb}_3\text{O}_4 + 4\text{HNO}_3 = 2\text{Pb(NO}_3)_2 + \text{H}_2\text{O} + \text{H}_2\text{PbO}_3$$
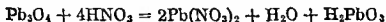
After the sample is dissolved, add 50 ml of $0.2 N$ oxalic acid, heat the solution to boiling, and titrate hot with $0.2 N$ KMnO$_4$. If t ml of $0.2 N$ KMnO$_4$ solution were used, then $50 - t$ ml of $0.2 N$ H$_2$C$_2$O$_4$ were necessary for the reduction of the amount of PbO$_2$ contained in the minium (a g) taken for analysis. There is present, therefore,

$$\frac{(50 - t) \times 2.392}{a} \text{ per cent PbO}_2 \text{ or } \frac{(50 - t) \times 6.856}{a} = \text{per cent Pb}_3\text{O}_4$$

The Diebl-Topf iodimetric method, described on p. 606, has been adopted by the American Society for Testing Materials for the analysis of red lead.

[1] Z. anal. Chem., 19, 153.

7. Determination of MnO_2 in Pyrolusite

$$1000 \text{ ml } N \text{ KMnO}_4 = \frac{MnO_2}{2} = 43.47 \text{ g } MnO_2$$

(a) Method of Levol and Poggiale, Modified by G. Lunge[1]

After drying at 120° to constant weight, place 1.087 g of the finely powdered pyrolusite in a 250-ml flask which is provided with a Contat valve (see p. 540). Expel the air by conducting CO_2 into the flask, and then add 75 ml of the ferrous sulfate solution, prepared as described below, close the flask, and heat its contents over a small flame until there is no longer any dark-colored residue. Cool quickly, dilute with 200 ml of water, and titrate the excess of ferrous sulfate with 0.5 N KMnO$_4$ solution. Immediately before the analysis, determine the titer of the ferrous sulfate solution by taking 25 ml of it, diluting to 200 ml, and titrating with permanganate.

By the treatment of the pyrolusite with ferrous sulfate, the following reaction takes place:

$$MnO_2 + 2Fe^{++} + 4H^+ \rightarrow Mn^{++} + 2Fe^{+++} + 2H_2O$$
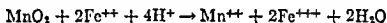
Prepare the ferrous sulfate solution as follows: Slowly pour 200 ml of concentrated sulfuric acid, with stirring, into 500 ml of water, and while the mixture is still hot add 100 g of powdered $FeSO_4 \cdot 7H_2O$ crystals; on stirring, the salt should dissolve within a few minutes. Dilute the solution to 1 l. When cold it is ready to use.

If 25 ml of $FeSO_4$ solution = a ml of N-normal KMnO$_4$, 75 ml of $FeSO_4$ solution used in the analysis and the excess = b ml of KMnO$_4$, then

$$\frac{(3a - b)N \times 0.01347 \times 100}{1.087} = \text{per cent } MnO_2$$

If the KMnO$_4$ is exactly 0.5 N, then $2(3a - b) = $ per cent MnO_2.

(b) Method of Fresenius-Will, Modified by Mohr

$$MnO_2 + C_2O_4^{--} + 4H^+ \rightarrow Mn^{++} + 2CO_2 + 2H_2O$$
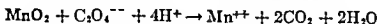
For each analysis, weigh out portions of the finely ground ore, which has been dried to constant weight at 120°, into 300-ml Erlenmeyer flasks, using samples that do not vary more than 0.05 g from 0.45 g. Add to each portion of ore a carefully weighed portion of pure sodium oxalate, using at least one and one-half times as much oxalate as pyro-

[1] *Chem. techn. Untersuchungsmethoden.*

lusite but not more than 0.8 g in any case. Add 50 ml of water and 50 ml of 6 N sulfuric acid and heat, without boiling hard, until no more pyrolusite remains undissolved. Keep the flasks covered with watch glasses, and do not allow the solutions to evaporate to less than 85 ml, adding hot water from time to time if necessary. When all the black ore has dissolved, dilute to 200 ml and titrate with 0.1 N permanganate, keeping the solution above 60°.

If s is the weight of pyrolusite used, r the weight of sodium oxalate, and n the milliliters of N normal permanganate required for the excess oxalate,

$$\left(\frac{r}{0.067 \times N} - n\right) \frac{N \times 0.0435 \times 100}{s} = \text{per cent } MnO_2$$

In this equation, 0.067 is the equivalent weight of sodium oxalate and 0.0435 the equivalent weight of manganese dioxide.

8. Determination of Formic Acid

(a) Method of Lieben[1]

$$1000 \text{ ml } N \text{ KMnO}_4 = \frac{3 \times \text{HCOOH}}{10} = 13.80 \text{ g HCOOH}[2]$$

In cold *acid* solutions permanganate reacts very slowly with formic acid, and in a hot solution the latter is lost by volatilization, so that the titration in open vessels is impossible; in *alkaline* solutions, on the other hand, the oxidation takes place readily and quantitatively in the cold:

$$2KMnO_4 + 3HCO_2K = 2K_2CO_3 + KHCO_3 + 2MnO_2 + H_2O$$

In this reaction the permanganate is reduced only to the quadrivalent condition so that it has only three-fifths of its oxidizing power as determined in the standardization. Hence the weight of formic acid equivalent to 1 ml of N permanganate (normal against sodium oxalate) is $\frac{3}{5} \times \frac{HCO_2H}{2000}$.

Procedure. Neutralize the formic acid by an excess of sodium carbonate, and allow permanganate to run into the hot sodium formate solution until the clear liquid above the precipitate is colored pink (cf. p. 550).

(b) Method of H. C. Jones[3]

$$1000 \text{ ml } N \text{ KMnO}_4 = \frac{HCO_2H}{2} = 23.01 \text{ g formic acid}$$

[1] *Monatsh.*, 14, 746, and 16, 219.
[2] *Ber.*, 10, 1075 (1877).
[3] *Am. Chem. J.*, 17, 539.

Add an excess of permanganate to the alkaline solution of the formate, heat 5–10 minutes on the water bath, make acid with $6 N$ sulfuric acid, add an excess of $0.1 N$ oxalic acid solution, and titrate the excess of oxalic acid with permanganate at $70°$.

If T = total volume of $0.1 N$ permanganate used and t the volume of $0.1 N$ oxalic acid then

$$(T - t)0.002301 = \text{weight of formic acid}$$

(c) Method of Blackadder[1]

Proceed exactly as in (b) but after heating on the water bath, add 2–3 g of potassium iodide, neutralize with $6 N$ hydrochloric acid, add 15 ml in excess, and titrate the liberated iodine with $0.1 N$ thiosulfate. If T is the volume of $0.1 N$ permanganate used and t the volume of $0.1 N$ thiosulfate, the computation is the same as under (b).

9. Analysis of Nitrous Acid (Lunge)[2]

$$1000 \text{ ml } N \text{ KMnO}_4 = \frac{\text{HNO}_2}{2} = \frac{47.018}{2} = 23.51 \text{ g HNO}_2$$

On account of the volatility of nitrous acid, measure out the aqueous solution of the nitrite, or the solution of nitrous acid in concentrated sulfuric acid (nitrose), from a buret into 400 ml of $0.75 N$ sulfuric acid containing a known volume of permanganate solution, warmed to $40°$. Have the tip of the buret dipping below the surface of the acid permanganate solution, and stir constantly. The nitrous acid is thereby oxidized to nitric acid:

$$2KMnO_4 + 5HNO_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5HNO_3$$
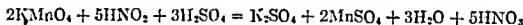
and the decolorization of the solution shows the end point. Toward the end the nitrous acid must be added slowly, for the change from red to colorless requires some time.

10. Analysis of Hydrogen Peroxide

$$1000 \text{ ml } N \text{ KMnO}_4 = \frac{H_2O_2}{2} = 17.01 \text{ g H}_2O_2$$

Place 10 ml of commercial 3 per cent hydrogen peroxide in a 100-ml measuring flask, dilute to the mark with water, and, after thoroughly mixing, transfer 10 ml (= 1 ml of the original solution) to a beaker,

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[1] Dissertation, Zürich, 1911.

[2] Ber., 10, 1075 (1877).

and dilute with water to a volume of 300–400 ml. After adding 20–30 ml 7.5 N sulfuric acid, titrate the solution with 0.1 N KMnO$_4$ until a permanent color pink is obtained. The following reaction takes place:

$$2KMnO_4 + 5H_2O_2 + 4H_2SO_4 = 2KHSO_4 + 2MnSO_4 + 8H_2O + 5O_2$$
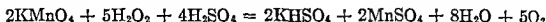
Frequently it happens that the first drop of the permanganate causes a permanent coloration of the solution. This shows that either not enough sulfuric acid is present, or else there is no more hydrogen peroxide left in the solution. In this case add a little more sulfuric acid, when, if the coloration still remains, the preparation is surely spoiled, as can be shown by the titanic or chromic acid tests (cf. Vol. I).

The amount of hydrogen peroxide is expressed either as percentage by weight or as percentage by volume.

Example. Ten milliliters of the above-mentioned dilute solution of hydrogen peroxide (= 1 ml of the original solution) required 17.86 ml of 0.1 N KMnO$_4$ solution, corresponding to 17.86 × 0.001701 = 0.03038 g H$_2$O$_2$. As the specific gravity of the original hydrogen peroxide solution can be assumed to be 1, it therefore contains 3.04 per cent H$_2$O$_2$.

When expressed in "percentage by volume" the result shows how many cubic centimeters of oxygen can be obtained from 100 ml of the solution.

In this case 100 ml of the hydrogen peroxide solution contains 3.04 g of H$_2$O$_2$ and, on being decomposed, 2 moles of H$_2$O$_2$ sets free 1 mole of O$_2$.

$$2H_2O_2 = 2H_2O + O_2$$
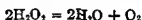
or 22.39 l of oxygen at 0°C and 760 mm pressure; consequently 3.04 g H$_2$O$_2$ will evolve $x = \dfrac{3.04 \times 11200}{34.02} = 1000$ ml oxygen measured under standard conditions of temperature and pressure.

One hundred milliliters of the commercial hydrogen peroxide, therefore, will evolve 1000 ml of oxygen, i.e., 10 times its own volume. This is sometimes designated as 10 volume hydrogen peroxide.

Other methods for determining hydrogen peroxide will be given later. (See Index.)

11. Analysis of Barium Peroxide

$$1000 \text{ ml } N \text{ KMnO}_4 = \frac{BaO_2}{2} = 84.68 \text{ g BaO}_2$$

Weigh 0.2 g of the substance into a 400-ml beaker, cover with 300 ml of cold water, and add with constant stirring, 20–30 ml of 2 N hydrochloric acid. When all the BaO$_2$ has dissolved, titrate the solution with 0.1 N KMnO$_4$. The addition of H$_2$SO$_4$ is not advisable, as the precipitated BaSO$_4$ is likely to enclose some BaO$_2$ which will then escape the titration.

Another method for the analysis of BaO_2 has been proposed by Kassner.[1]

12. Analysis of Potassium Percarbonate

$$1000 \text{ ml } N \text{ KMnO}_4 = \frac{K_2C_2O_6}{2} = 99.10 \text{ g } K_2C_2O_6$$

Weigh 0.25 g of potassium percarbonate into 300 ml of cold, N sulfuric acid, in which it dissolves with vigorous evolution of carbon dioxide and formation of an equivalent amount of hydrogen peroxide:

$$K_2C_2O_6 + 2H_2SO_4 = 2KHSO_4 + 2CO_2 + H_2O_2$$

Titrate the latter with 0.1 N potassium permanganate.

13. Analysis of Persulfates (Persulfuric Acid, $H_2S_2O_8$)

$$1000 \text{ ml } N \text{ KMnO}_4 = \frac{R_2S_2O_8}{2} \begin{cases} 97.07 \text{ g } H_2S_2O_8 \\ 114.1 \text{ g } (NH_4)_2S_2O_8 \\ 135\ 2 \text{ g } K_2S_2O_8 \end{cases}$$

A solution of persulfuric acid does not reduce permanganate, nor does it react with titanic acid; on the other hand it oxidizes ferrous salts immediately in the cold to ferric salts, and by means of this behavior it can be easily determined. The ammonium and potassium salts are now commercial products, and are analyzed as follows: Weigh 0.3 g of the salt into a flask fitted with a Bunsen valve (p. 540), replace the air by carbon dioxide, add 30 ml of a freshly titrated solution of ferrous sulfate and then 200 ml of hot water. Close the flask and rotate its contents. The salt dissolves without difficulty, and the ferrous sulfate is oxidized:

$$H_2S_2O_8 + 2FeSO_4 = Fe_2(SO_4)_3 + H_2SO_4$$
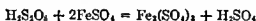
After all the salt has dissolved, cool the contents of the flask by placing the flask in cold water, and titrate the excess of ferrous salt with 0.1 N KMnO₄.

The ferrous sulfate must be added to the persulfate, and then the hot water. If the hot water is added first, the persulfate is decomposed somewhat and the results obtained will be low. In this way it is found that:

30 ml ferrous sulfate solution requires T ml 0.1 N KMnO₄ solution.

30 ml ferrous sulfate + a g persulfate requires t ml 0.1 N KMnO₄ solution.

Consequently a g of persulfate correspond to $(T - t)$ ml 0.1 N KMnO₄.
In the case of the potassium salt, since 1000 ml N KMnO₄ = 135.2 g $K_2S_2O_8$, and 1 ml 0.1 N KMnO₄ = 0.01352 g $K_2S_2O_8$, we have: $(T - t) \times 0\ 01352$ g $K_2S_2O_8$ in a g of the commercial salt, or in percentage: $\dfrac{1.352\ (T - t)}{a}$ = per cent $K_2S_2O_8$.
With the ammonium salt the factor becomes 0 01141 instead of 0 01352.

The ferrous sulfate necessary for this determination is prepared as described on p. 579.

[1] *Arch. Pharm.*, 228, 432.

Persulfates may also be analyzed very satisfactorily by means of oxalic acid.[1] When a sulfuric acid solution of a persulfate is treated with oxalic acid alone, there is no perceptible reaction. On adding a small amount of silver sulfate as catalyzer, however, a lively evolution of carbon dioxide takes place, and at the water-bath temperature the reaction is soon completed.

$$H_2S_2O_8 + H_2C_2O_4 = 2H_2SO_4 + 2CO_2$$
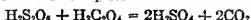
The excess of the oxalic acid can be titrated with permanganate.

Procedure. Place 0.5 g of the persulfate in a 400-ml Erlenmeyer flask; add 50 ml of 0.1 N oxalic acid solution and 0.2 g of silver sulfate dissolved in 20 ml of 10 per cent sulfuric acid. Heat the mixture on the water bath until the evolution of carbon dioxide ceases; this requires not more than 15 or 20 minutes. Dilute the solution to about 100 ml with water at about 40° and titrate with 0.1 N permanganate.

14. Determination of Hydroxylamine (Raschig)[2]

$$1000 \text{ ml } N \text{ KMnO}_4 = \frac{NH_2OH}{2} = 16.52 \text{ g } NH_2OH$$

Principle. Hydroxylamine is oxidized in hot acid solution by means of ferric salts to form nitrous oxide and an equivalent amount of ferrous salt:

$$2NH_2OH + 4Fe^{+++} \rightarrow 4Fe^{++} + N_2O + 4H^+ + H_2O$$
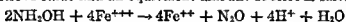
The quantity of ferrous salt is determined by titration with 0.1 N potassium permanganate.

Procedure. Place 0.1 g of the hydroxylamine salt in a 500-ml flask and dissolve in a little water. Add 30 ml of a cold, saturated solution of ferric-ammonium alum and 10 ml of 7.5 N sulfuric acid. Heat the contents of the flask to boiling and keep at this temperature for 5 minutes. Then dilute the solution with distilled water to a volume of about 300 ml and immediately titrate with permanganate solution.

Remark. If only slightly more than the theoretical amount of the ferric salt is added, the oxidation of the hydroxylamine does not take place entirely in accordance with the above equation, but part of the substance is oxidized to nitric oxide:

$$2NH_2OH + 6Fe^{+++} \rightarrow 6Fe^{++} + 2NO + 6H^+$$
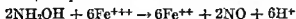
and it is then impossible to obtain exact results.

15. Determination of Ferrocyanic Acid (De Haën)[3]

$$1000 \text{ ml } N \text{ KMnO}_4 = 1 \text{ mole } K_4Fe(CN)_6 = 422.4 \text{ g } K_4Fe(CN)_6 \cdot 3H_2O$$

Principle. By oxidation in acid solution, ferricyanic acid is formed from ferrocyanic acid:

$$5H_4Fe(CN)_6 + MnO_4^- + 3H^+ \rightarrow 5H_3Fe(CN)_6 + Mn^{++} + 4H_2O$$

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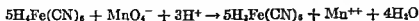
[1] R. Kempf, *Ber.*, **38**, 3965 (1905).

[2] *Ann. Chem. Pharm.*, **241**, 318.

[3] *Ibid.*, **90**, 160.

Good results are obtained only when the solution is dilute and contains considerable acid. If too much ferrocyanide is present, a precipitate of $K_2Mn[Fe(CN)_6]$ is likely to form. In this case it is necessary to make sure that sufficient acid is present and to dilute the solution. The end point is a change from greenish yellow to yellowish pink.

Procedure. Dissolve 10 g of potassium salt in 1 l of water. Mix and transfer 50 ml to a white porcelain dish. Add 100–150 ml of water and 10–20 ml of 7.5 N sulfuric acid and titrate with 0.1 N permanganate.

16. Determination of Ferricyanic Acid

$$1000 \text{ ml } N \text{ KMnO}_4 = 1 \text{ mole } K_3Fe(CN)_6 = 329.2 \text{ g } K_3Fe(CN)_6$$

Principle. The potassium ferricyanide is reduced in alkaline solution to potassium ferrocyanide, which is titrated with permanganate.

Procedure. In a 300-ml measuring flask dissolve 6.0 g of the ferricyanide in water, make the solution alkaline with potassium hydroxide, heat to boiling, and add an excess of a concentrated ferrous sulfate solution. At first brown ferric hydroxide is precipitated, later black ferrous-ferric hydroxide is formed, and this shows the completion of the reaction. Cool, dilute the contents of the flask with water to the mark, filter through a dry filter (after mixing), reject the first runnings, and take 50 ml of the filtrate (= 1 g of the substance) for the titration with 0.1 N MnO$_4$ solution.

17. Determination of Chloric Acid

$$1000 \text{ ml } N \text{ KMnO}_4 = \frac{RClO_3}{6} = \begin{cases} 20.43 \text{ g } KClO_3 \\ 17.74 \text{ g } NaClO_3 \end{cases}$$

Dissolve 5 g of potassium chlorate, or 4 g of the sodium salt, in water, and dilute the solution to 1 l. After thoroughly mixing, transfer 10 ml to a flask fitted with a Bunsen valve (p. 540) and expel the air from the flask by a current of carbon dioxide. After this add 50 ml of a freshly standardized 0.1 N solution of ferrous sulfate in 2.5 N H_2SO_4 and boil the solution 5 minutes. The following reaction takes place:

$$KClO_3 + 6FeSO_4 + 3H_2SO_4 = KCl + 3Fe_2(SO_4)_3 + 3H_2O$$
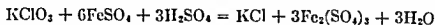
After cooling, dilute the solution with cold distilled water to 200 ml, add 10 ml of manganous sulfate solution (cf. p. 545), and titrate the excess of the ferrous sulfate with potassium permanganate.

If 50 ml ferrous sulfate . . . . required T ml 0.1 N KMnO$_4$ sol.
and 50 ml   "   "   + 10 ml chlorate sol.   " t ml 0.1 N "   "
then 10 ml of chlorate solution = 0.01 a g   = $(T - t)$ ml 0.1 N KMnO$_4$ "
where a = original weight of the sample.

The substance contains $\dfrac{20.43 \times (T - t)}{a}$ per cent of KClO$_3$

18. *Determination of Nitric Acid* (Pelouze-Fresenius)

$$1000 \text{ ml } N \text{ KMnO}_4 = \frac{\text{RNO}_2}{3} \begin{cases} 21.01 \text{ g HNO}_3 \\ 28.34 \text{ g NaNO}_3 \\ 33.70 \text{ g KNO}_3 \end{cases}$$

This method depends upon the fact that on heating a nitrate with an acid ferrous chloride solution the nitric acid is reduced to nitric oxide:

$$2KNO_3 + 6FeCl_2 + 8HCl = 2KCl + 2NO + 4H_2O + 6FeCl_3$$
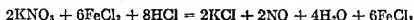
As a measure for the amount of nitrate reduced we have:

(1) The excess of ferrous salt. (2) The ferric salt produced. (3) The nitric oxide formed.

The method of Schlösing-Grandeau described on p. 386 is based upon the measurement of the nitric oxide formed. C. D. Braun[1] estimates the amount of ferric salt formed, while Pelouze and Fresenius determine the amount of ferrous salt not used up in the reduction of the nitric acid.

Procedure. Place 1.5 g of pure iron wire in a long-necked flask, and expel the air by passing a current of pure carbon dioxide through it for 2–3 minutes. Then add 30–40 ml of concentrated hydrochloric acid, place the flask in an inclined position, and close by means of a rubber stopper through which tubes pass so that a current of carbon dioxide can be introduced. Heat the solution on the water bath in this atmosphere of carbon dioxide until the iron has completely dissolved, and allow the solution to cool in a current of the gas. Meanwhile weigh 0.25–0.3 g of the nitrate into a small glass tube closed at one end. Drop this into the acid solution of the ferrous sulfate and quickly close the flask again. Heat as before for 15 minutes, while continuing the stream of carbon dioxide. Have the exit tube through from the flask dipping into a beaker filled with water so that there is no chance of any air getting back into the flask. Finally heat the solution to boiling and keep hot until the dark color disappears and the yellow color of the ferric chloride becomes apparent. To make sure that the nitric oxide is entirely removed boil 5 minutes longer and then allow to cool in the atmosphere of carbon dioxide. When cold pour the solution into a beaker, rinse the flask with a little boiled water, and dilute to about 400 ml. Add 10 ml of manganese sulfate solution (p. 545), and titrate the unoxidized ferrous salt with 0.5 N KMnO₄ solution.

Determine the purity of the iron wire by titrating 1 g of the wire after similar treatment with acid and manganese sulfate solution.

If *a* g of potassium nitrate and *p* g of the wire were taken for the analysis, *t* ml of 0.5 KMnO₄ was required to oxidize the excess of iron,

[1] *J. prakt. Chem.*, 81, 421 (1860).

and p g of the wire requires T ml of 0.5 KMnO$_4$, then:

$$\frac{(T - t) \times 1.685}{a} = \text{per cent } KNO_3$$

Remark. This method gives results just as accurate as those obtained by the method of Devarda (p. 384) and is much easier to carry out.

19. Determination of Vanadic Acid

$$1000 \text{ ml of } 0.1 \text{ N KMnO}_4 = \frac{V_2O_5}{20} = 9.095 \text{ g } V_2O_5$$

Conduct sulfur dioxide into the boiling acid solution of an alkali vanadate until the solution is clear blue in color; by this means the vanadic acid is reduced to vanadyl salt:

$$2H_3VO_4 + H_2SO_3 + H_2SO_4 \rightarrow V_2O_2(SO_4)_2 + 5H_2O$$

$$5V_2O_2^{++++} + 2MnO_4^- + 22H_2O \rightarrow 10H_3VO_4 + 2Mn^{++} + 14H^+$$
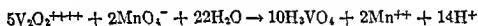
Continue boiling and introduce a current of carbon dioxide through the solution until the escaping gas will no longer decolorize a solution of potassium permanganate, showing that the excess of the sulfur dioxide has been expelled. Titrate the hot solution with potassium permanganate until a permanent pink color is obtained. The end point is easily recognized only when the solution is hot. This accurate determination is used for the analysis of vanadium in iron and steel, or in ores. (Cf. pp. 242, 570.)

20. Blair Method for Determining Phosphorus in Steel[1]

$$1000 \text{ ml of } 0.1 \text{ N KMnO}_4 = \frac{P}{360} = 0.0883 \text{ or } 0.0861 \text{ g } P$$

Transfer the yellow precipitate obtained as described on p. 516 or p. 517 to a paper filter but, instead of the 1 per cent HNO$_3$ and 1 per cent KNO$_3$ solutions, use an acid ammonium sulfate solution (1 l of water, 25 ml concentrated H$_2$SO$_4$, and 15 ml strong ammonia; mix well before using). Wash the precipitate promptly with ten 5-ml portions of this acid sulfate solution, wetting the upper edge of the filter paper each time and allowing each portion to drain through the filter paper before adding the next.

Dissolve the ammonium phosphomolybdate precipitate in 25 ml of 3 N ammonium hydroxide, wash the filter with hot water, and treat the filtrate with 10 ml of concentrated sulfuric acid. It is now ready for

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[1] Andrew Blair, *The Chemical Analysis of Iron and Steel.*

reduction with the Jones reductor (see p. 544). Run a blank with the reductor before each series of determinations and whenever the reductor has stood idle for 3 hours. After a reductor has stood over night, it should be well washed with dilute sulfuric acid, before even a blank test is run. Titrate the reduced solution with permanganate.

In making blanks and in all determinations, the procedure is as follows. Add 100 ml of normal sulfuric acid through the funnel, B, with the stopcock C open, using a little suction. When only a little of the dilute acid remains in the funnel, add the solution to be reduced or, for blanks, 50 ml of 1.5 N sulfuric acid, and when this has nearly passed out of the funnel, follow with 250 ml of normal sulfuric acid, washing out the original beaker with this acid and adding it in small portions. Finally, pass 100 ml of water through the reductor and titrate in the permanganate. Air should not be allowed to enter the reductor tube, which should be kept full of water at all times when idle. Run blanks until two successive tests require less than 0.2 ml of 0.1 N permanganate to give a pink color to the acid solution.

In the original method, the reduced solution was caught in an empty flask and it was assumed that the MoO₃ of the phosphomolybdate precipitate was reduced completely to the trivalent condition by the amalgamated zinc:

Mo_2O_3; 1 ml of 0.1 N $KMnO_4$ = 0.0000883 g P. The molybdenum is reduced completely to the trivalent condition by the amalgamated zinc:

$$(NH_4)PO_4 \cdot 12MoO_3 + 23NH_4OH = 12(NH_4)_2MoO_4 + (NH_4)_2HPO_4 + 11H_2O$$
$$2MoO_4^{--} + 3Zn + 16H^+ \rightarrow 2Mo^{+++} + 3Zn^{++} + 8H_2O$$
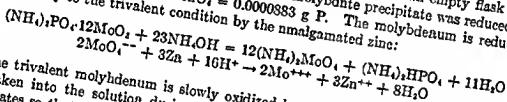
The trivalent molybdenum is slowly oxidized by the air in the flask and by that shaken into the solution during the titration. A practiced manipulator usually titrates so that about 3 per cent of the total oxidation is accomplished by the air, and this corresponds to the assumption that Blair made with respect to the hypothetical Mo₂O₃₇. The only safe way to avoid this error is to catch the reduced solution, before it comes in contact with air, in 50 ml of 10 per cent ferric alum solution (100 g of ferric alum, 25 ml of concentrated sulfuric acid, and 40 ml of sirupy phosphoric acid per liter). Then 1 ml of 0.1 N $KMnO_4$ = 0.0000861.

This ferric alum solution does not change the reduced molybdenum entirely back to the 6-valent condition but it does oxidize it sufficiently to prevent the effect of the atmosphere, and for every equivalent of molybdenum oxidized an equivalent of reduced iron is formed so that the solution titrates exactly as if a perfect reduction were obtained without the use of the ferric salt. Since the precipitate contains 1P:12Mo, and the valence change of the Mo is 3, it is clear how the normal weight is computed. When this ferric alum solution is used in the analysis, it must be present also in running the blanks.

To illustrate the computation assume that the ammonium phosphomolybdate precipitate from 2 g of steel required by the above method 12 ml of 0.1 N permanganate solution. The blank on the reductor and ferric alum was 0.18 ml. The phosphorus present in the steel is then: (12 − 0.18) × 0.00431 per cent.

If 2.15 g of steel is taken for analysis, the percentage of phosphorus will be 0.004 times the net volume of 0.1 N permanganate in milliliters when ferric alum is used.

21. Chromium in Steel

Chromium, when present as trivalent chromic cations, behaves like ferric iron toward many reagents. Practically all methods for determining chromium in iron and steel are based upon its oxidation to the positive valence of 6 as chromic acid, dichromate, or chromate. Small quantities of chromium can be determined colorimetrically, but quantities larger than a few hundredths of 1 per cent are usually determined by adding a measured volume of reducing agent, usually acid ferrous sulfate solution, and titrating the excess with potassium permanganate solution. A great many different methods have been proposed for carrying out the oxidation, but treatment with ammonium persulfate in the presence of silver ions as catalyst has been found most convenient. If vanadium is present, it can be determined in the same solution after the chromium.

Determination of Chromium and Vanadium in Alloy Steel[1]

In this procedure the manganese, chromium, and vanadium are first obtained in the bivalent, trivalent, and quadrivalent states respectively by dissolving in acid. By the action of persulfate in the presence of silver salt as catalyzer, the bivalent manganese is oxidized to the valence of 7, the trivalent chromium to the valence of 6, and the quadrivalent vanadium to the valence of 5. By the addition of a limited quantity of chloride, the permanganic acid is reduced to manganous salt and the excess persulfate is removed by boiling. The chromic acid is then reduced to chromic salt by a measured quantity of ferrous solution, and the excess titrated with permanganate. The chromium content corresponds to the amount of ferrous salt required. The vanadium, to be sure, is reduced to vanadyl salt by the ferrous iron but is again oxidized to vanadic acid by the permanganate so that it affects the analysis only by making the end point a slow one.

After the titration, all manganese is present as manganous salt, all chromium as chromic salt, and all vanadium as vanadate. Another portion of ferrous salt serves to reduce the vanadium to quadrivalent vanadyl salt. The excess ferrous iron can be oxidized by stirring with persulfate solution without oxidizing the vanadium, and the vanadyl salt can be titrated with permanganate.

The important chemical reactions involved can be expressed by the following equations:

Oxidation with persulfate in the presence of Ag^+ ions:

$$2Cr^{+++} + 3S_2O_8^{--} + 8H_2O \rightarrow 2H_2CrO_4 + 6SO_4^{--} + 12H^+$$
$$2VO^{++} + S_2O_8^{--} + 4H_2O \rightarrow 2HVO_4 + 2SO_4^{--} + 6H^+$$
$$2Mn^{++} + 5S_2O_8^{--} + 8H_2O \rightarrow 2HMnO_4 + 10SO_4^{--} + 14H^+$$
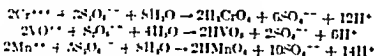
Removal of the catalyzer and reduction of $HMnO_4$:

$$Ag^+ + Cl^- \rightarrow AgCl$$
$$2HMnO_4 + 14H^+ + 10Cl^- \rightarrow 2Mn^{++} + 8H_2O + 5Cl_2$$

Reduction with $FeSO_4$:

$$Cr_2O_7^{--} + 6Fe^{++} + 14H^+ \rightarrow 2Cr^{+++} + 6Fe^{+++} + 7H_2O$$
$$HVO_4 + Fe^{++} + 3H^+ \rightarrow VO^{++} + Fe^{+++} + 2H_2O$$
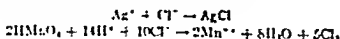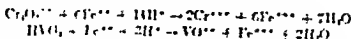
[1] Procedure based on *Methods of the Chemists of the United States Steel Corporation*.

Titration with $KMnO_4$:

$$5Fe^{++} + MnO_4^- + 8H^+ \rightarrow 5Fe^{+++} + Mn^{++} + 4H_2O$$
$$5VO^{++} + MnO_4^- + 6H_2O \rightarrow 5HVO_3 + Mn^{++} + 7H^+$$
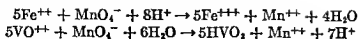
Reduction with $FeSO_4$ the second time:

$$HVO_3 + Fe^{++} + 3H^+ \rightarrow VO^{++} + Fe^{+++} + 2H_2O$$
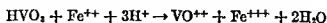
Removal of excess $FeSO_4$ the second time:

$$2Fe^{++} + S_2O_8^{--} \rightarrow 2Fe^{+++} + 2SO_4^{--}$$

Final titration:

$$5VO^{++} + MnO_4^- + 6H_2O \rightarrow 5HVO_3 + Mn^{++} + 7H^+$$
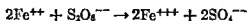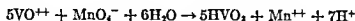
Procedure. Weigh out 2 g of sample, or less if more than 2 per cent of chromium is present, into a 600-ml beaker, and cover it with a mixture of 45 ml water, 10 ml concentrated sulfuric acid, and 5 ml of phosphoric acid, d 1.7. Heat until there is no further action, add 5 ml of concentrated nitric acid, and boil to decompose carbides and oxidize the iron. (If carbides resist this treatment, as shown by considerable dark-colored residue, or tungsten is present as shown by a yellow residue of WO_3, evaporate until salts begin to separate out, dilute with 50 ml of water, add 10 ml of concentrated HNO_3, and again evaporate.) Add 200 ml of water, filter, and wash the residue with water. To the filtrate add 10 ml of 0.1 N silver nitrate, heat nearly to boiling, and add slowly while stirring 20 ml of freshly prepared 15 per cent ammonium persulfate solution. If a permanganate color does not develop from the manganese in the steel, heat again and add more silver nitrate and more persulfate. Then boil 8–10 minutes to decompose the excess persulfate, add 2 ml of 6 N hydrochloric acid, and heat 5 minutes after the permanganate color, or any precipitated manganese dioxide, has disappeared. Dilute to 400 ml, add 25 ml of 0.1 N ferrous ammonium sulfate solution from a pipet (p. 576), and test a drop of the solution on a white porcelain spot plate with a freshly prepared solution of potassium ferricyanide. If the blue test is not obtained, add another portion of ferrous salt. Titrate the excess with 0.1 N permanganate until the pink end point persists after stirring for 1 minute.

In this analysis a perceptible excess of permanganate is required because of the dilution and the color of the chromic salt. To allow for this error, assume that the milliequivalent of chromium is 0.01744 instead of the theoretical value. The end point is a little difficult because of the slow rate of oxidation of the vanadium in cold, dilute solutions.

Determination of Vanadium. After the chromium determination, add 5 ml of standard ferrous ammonium sulfate solution from a pipet. Stir and test a drop of the solution for ferrous iron with fresh ferricya-

nide solution, adding another pipetful of ferrous salt if necessary. Add 8 ml of 15 per cent ammonium persulfate solution and stir 1 minute to oxidize the excess of ferrous salt. Then titrate with permanganate till the end point persists after 1 minute's stirring. In this case, the vanadium is titrated directly and 1 ml of 0.1 N permanganate oxidizes 0.005095 g of vanadium. The error due to dilution and color of the chromic ions is positive. From the percentage of vanadium found, subtract 0.02 plus 0.018 times the percentage of chromium in the sample.

22. Determination of Molybdenum in Wulfenite and Molybdenite[1]

1. Method of Dissolving Wulfenite

Dissolve 1 g of the powdered ore by treatment with 15 ml of concentrated nitric acid and 7 ml of concentrated sulfuric acid in a 150-ml covered beaker at a temperature just short of boiling. When practically complete decomposition has been effected, evaporate until fumes of sulfur trioxide are expelled freely. .Cool, add 40 ml of water, boil to dissolve the bulk of the molybdenum, cool to tap-water temperature, and filter into a 150-ml beaker; the residue consists of lead sulfate, silica, and possibly small amounts of undecomposed ore, and tungstic and molybdic acids. Save both the residue and the filtrate.

Dissolve the lead sulfate in hot ammonium acetate solution (see p. 59), washing until the ammonium acetate filtrate gives no test for lead with ammonium sulfide solution. Ignite the silicious residue in a platinum crucible and remove silica by treating it with sulfuric and hydrofluoric acids. Evaporate till all the excess acid is expelled. If an appreciable residue remains after this treatment, fuse it with potassium pyrosulfate and test for molybdenum by means of tartaric acid and ammonium sulfide as further described. The residue, however, seldom contains any molybdenum.

2. Method of Dissolving Molybdenite

Treat 0.5–5 g of the finely pulverized sample with 10–35 ml of concentrated nitric acid and 7–10 ml of concentrated sulfuric acid in a 250-ml beaker, covered with a watch glass. Digest at a temperature somewhat below the boiling point until most of the molybdenite appears to have been decomposed, and then evaporate until strong fumes of sulfur trioxide are evolved. When the beaker and its contents have cooled, add 50 ml of water and boil briskly for a few minutes. Filter

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[1] Method furnished by the Bureau of Standards and based upon the work of J. A. Holladay and A. M. Smoot.

into a 150-ml beaker. Wash the residue with hot water, then 6 or 8 times with $4\ N$ ammonium hydroxide, and finally with hot water, allowing the washings to run into the main filtrate.

Treat the silicious residue (which will also contain nearly all lead and barium present in the ore) with ammonium acetate solution (cf. p. 59) and ignite the remainder at a very low red heat in a porcelain crucible, cool, transfer to a platinum crucible, treat with 2 or 3 drops of concentrated sulfuric acid and several milliliters of hydrofluoric acid, and evaporate until sulfuric acid has been completely expelled. Fuse the small residue remaining with sodium carbonate, extract with water, and add the water extract to the main solution.

3. Method of Analysis

To the solution containing all the molybdenum, add sufficient ferric sulfate to provide 10 times as much iron as there is arsenic present; from 0.3 to 0.4 g is usually ample. Nearly neutralize the acid with ammonia (do not add enough to impart a red tint to the solution), heat nearly to boiling, and pour slowly and with vigorous stirring into 75 ml of nearly boiling $9\ N$ ammonium hydroxide contained in a 250-ml beaker. When the precipitate has settled, filter and wash thoroughly with hot water. Dissolve the precipitate in a slight excess of hot $7.5\ N$ sulfuric acid, heat to boiling, and pour again into 75 ml of boiling $9\ N$ ammonium hydroxide. Collect the two filtrates, containing all the molybdenum, in a 500-ml beaker. It is essential that arsenic, which is usually present in these ores, be eliminated, and the method described furnishes a simple and effective way for accomplishing this. The addition of ferric sulfate should be omitted only if arsenic is known to be absent.

To the combined ammoniacal filtrates, add 3 g of tartaric acid, and when the acid has dissolved, saturate the warm solution with hydrogen sulfide. The presence of tartaric acid is necessary to prevent the subsequent precipitation of vanadium and tungsten sulfides. If these elements are known to be absent its use may be dispensed with. Under these conditions the molybdenum remains in solution as ammonium thiomolybdate, $(NH_4)_2MoS_4$, which imparts a deep red color to the solution. If a small precipitate of insoluble sulfides separates out, filter and wash with hydrogen sulfide water. Make the thiomolybdate solution *slightly acid* with sulfuric acid (cf. p. 114).

Heat for a short time, allow the precipitate to settle, filter, and wash thoroughly with hydrogen sulfide water containing a little sulfuric and tartaric acids.

The filtrate from the molybdenum sulfide sometimes contains appreciable amounts of molybdenum.

Boil off the hydrogen sulfide, add an excess of bromine water to oxidize molybdenum, expel the excess by boiling, make ammoniacal as before, and treat with hydrogen sulfide and acid as outlined on p. 114. If any more molybdenum sulfide is formed, recover it.

Place the molybdenum sulfide precipitate and filter paper in a 250-ml flask and treat with 6 ml of concentrated sulfuric acid and 10 ml of concentrated nitric acid. Evaporate to fumes and repeat the nitric acid treatment, evaporating until the filter paper has been completely destroyed and every trace of yellow color due to carbonaceous matter has disappeared. When this has been accomplished, allow the solution to fume strongly for a short while, cool, add 5 ml of water, and again evaporate to fumes to ensure the expulsion of every trace of nitric acid. Cool, add 75 ml of water, and boil for a few minutes, which should give a perfectly clear solution. Add 5 g of pure shot zinc (0.002 per cent iron or under), and boil the solution until most of the zinc has dissolved; this results in partial reduction of the molybdenum and complete precipitation of the traces of copper which are usually present. Filter on an asbestos or Alundum filter to remove the undissolved zinc and the copper.

Reduce the molybdenum completely as described on p. 568 and titrate with 0.1 N permanganate; 1 ml 0.1 N permanganate solution = 0.003198 g of molybdenum.

23. Determination of Titanium[1]

1000 ml 0 1 N KMnO$_4$ = 0.1 gram-atom Ti = 4.790 g Ti

Principle. The reduction of titanium from the quadrivalent to trivalent condition proceeds rapidly and quantitatively in 1.1 to 1.8 N H$_2$SO$_4$ solution by passage through n Jones reductor. Organic compounds, nitric acid, tin, arsenic, antimony, molybdenum, iron, chromium, vanadium, tungsten, uranium, and columbium must be absent but, with the exception of the rare element columbium, all these can be easily separated from titanium. Nitric acid can be removed by repeated evaporation with sulfuric acid. Arsenic, antimony, and tin can be removed as sulfides from a solution sufficiently acid to prevent hydrolysis of the titanium. Iron can be precipitated as sulfide from an alkaline tartrate solution (see p. 168), and the organic matter then removed by treatment with nitric and sulfuric acids. Chromium, vanadium, tungsten, and uranium can be removed by oxidation in alkaline solution with sodium peroxide and boiling to precipitate titanium hydroxide.

Procedure. Carry out the reduction as described on p. 568 for molybdenum, taking the precaution to wash out the reductor with

[1] G. F. Lundell and H. B Knowles, *J. Am. Chem. Soc.*, 45, 2620 (1923).

dilute sulfuric acid before each run, which is carried out in the following order: 25 to 50 ml of 1.1–1.8 N sulfuric acid, 150 ml of the same strength acid containing 0.12 g of titanium or less, 100 ml more of acid, and finally 100 ml of water. Catch the solution in 3 times the theoretical quantity of ferric sulfate dissolved in 3 N sulfuric acid, and titrate the ferrous sulfate solution with permanganate. The reduction takes place at any temperature between 25° and 100°, and it is not necessary to expel air from the solutions used in the reductor.

$$2Ti^{++++} + Zn \rightarrow 2Ti^{+++} + Zn^{++}$$

$$Ti^{+++} + Fe^{+++} \rightarrow Fe^{++} + Ti^{++++}$$
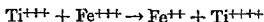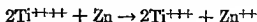
Rapid Volumetric Determination of Titanium in Ores

The following procedure has proved useful for the rapid evaluation of ores and titanium products.

Weigh out about 0.5 of the finely powdered sample into a dry, heavy-walled, 8-in. test tube and mix it with about 7 g of powdered $K_2S_2O_7$ (made by fusing $KHSO_4$ to a quiet melt from which SO_3 is beginning to escape, pouring out upon a tile, and powdering). Tap the sides of the tube to drive down adhering particles, and clamp the tube in a vertical position but fixed so that later it can be swung to a nearly horizontal position. Heat the mass gently until the flux has melted and all water has been expelled. When an orange coloration is seen at the sides of the tube near the surface of the melt, raise the temperature gradually to redness and continue fusing until there are no more bubbles rising from the bottom and all the solid particles of ore have disappeared. Then heat any portion of the tube where there is evidence of spattering. By changing the position of the clamp, raise the bottom of the tube and allow the melt to flow halfway up the sides of the tube; clamp the tube in this nearly horizontal position. In a few minutes the mass will solidify and the melt will usually crack so that it can be dislodged from the tube with the aid of a steel spatula.

Add to the tube 30 ml of 18 N H_2SO_4 and heat until the melt has dissolved to a clear solution, in which the titanium is present as $Ti(SO_4)_2$. Disregard a slight turbidity which may be silica or a difficultly soluble sulfate. If any TiO_2 forms by hydrolysis, it can usually be distinguished by its relatively high index of refraction and appears as sharply contrasted white clots. These can usually be dissolved by adding 2 ml of concentrated H_2SO_4 and boiling gently. Sometimes it is necessary to discard the sample.

Dilute the solution to about 250 ml and pass through a Jones reductor

as described on p. 568, but use very little suction and have a piece of marble weighing about 5 g in the flask to provide an atmosphere of CO_2, but with no ferric sulfate solution in the flask. First pass 50 ml of 3–5 per cent H_2SO_4 through the cleaned and tested reductor containing amalgamated zinc (cf. p. 574), then the titanium solution, then 100 ml more of 3–5 per cent acid, and finally 100 ml of water. Remove from the reductor, add 5 ml of 20 per cent KCNS solution, and titrate with standard ferric alum solution until noticeable red color of $Fe(CNS)_3$ is permanent for 90 seconds. Run a blank to determine how much of the ferric alum solution is necessary to give an end point with 500 ml of 3 per cent H_2SO_4 and 5 ml of the indicator. To prepare the ferric alum solution, dissolve 50 g of $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$ in 1 l of 0.5 N H_2SO_4, and standardize by the above procedure against 0.2-g portions of pure TiO_2.

$$Ti^{+++} + Fe^{+++} \rightarrow Ti^{++++} + Fe^{++}$$

$$Fe^{++} + 3CNS^- \rightarrow Fe(CNS)_3 \quad \text{red end point}$$
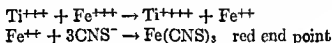
B. POTASSIUM DICHROMATE METHODS

1. Determination of Iron according to the Method of Penny

Potassium dichromate is one of the well-known oxidizing agents used in volumetric analysis. It reacts, for example, with ferrous, stannous, or titanous salts and is reduced, thereby, to trivalent chromic salt. Equations for the reduction of the dichromate ion and oxidation of ferrous ion, etc., have been given on p. 450. Expressed in terms of electrons, e, the equation for the reduction of dichromate can be written

$$Cr_2O_7^{--} + 14H^+ + 6e \rightleftharpoons 2Cr^{+++} + 7H_2O$$

and that of the oxidation of ferrous ion

$$Fe^{++} - e \rightleftharpoons Fe^{+++}$$

These equations represent what actually takes place when the reduction of the dichromate is accomplished at the cathode and the oxidation of the iron is brought about at the anode of an electrolytic cell. There are 6.06×10^{23} actual atoms of iron in a gram atom, and if we multiply the actual charge of the electron by 6.06×10^{23} we obtain the value 96,500 coulombs which is called a *faraday*. When 6 faradays of electricity pass through an electrolytic cell containing an acid solution of dichromate at the cathode and a ferrous salt at the anode, 1 mole of dichromate can be reduced and 6 moles of ferrous iron can be oxidized. The above equations, therefore, show that the equivalent weight of dichromate is one-sixth of its molecular weight and that of ferrous ion is one atomic weight.

Preparation and Standardization of Dichromate Solution

Prepare an approximately tenth-normal solution of potassium dichromate by dissolving not more than 5 g of the salt in water and diluting the solution to the volume of about 1 l.[1]

Prepare an approximately tenth-normal solution of ferrous ammonium sulfate by mixing 40 g of the crystals with 50 ml of 6 N sulfuric acid and diluting to about 1 l. The ferrous ions in this solution oxidize slowly from atmospheric oxygen that dissolves in the solution. The acid is necessary, therefore, to keep the salt in solution since the original salt contains acid combined with bivalent ferrous ions and not enough for the trivalent iron formed by oxidation. The strength of this solution will diminish slowly from day to day. The dichromate solution, on the other hand, is very stable.

To determine the relative strengths of the two solutions, fill a glass-stoppered buret with the dichromate solution, observing the usual precautions with respect to cleaning and rinsing, and fill a plain buret with the ferrous solution. Or, since the relative strengths of the two solutions change slightly from day to day and the determination may have to be repeated frequently, it is somewhat more convenient to use a 25-ml pipet for the ferrous solution, cleaning the pipet carefully (see p. 442) and rinsing it with three portions of the solution.

Run out from the buret about 40 ml of the ferrous solution into a beaker or flask of about 300-ml capacity. Add 10 ml of 6 N hydrochloric acid and 100 ml of water. Mix and titrate with the potassium dichromate solution.

Determination of the End Point. The end point of this titration can be determined in three ways: (1) by means of an external indicator, (2) by an internal indicator, and (3) by the potentiometer.

(1) The end point of the titration of ferrous ions with dichromate can be determined by taking a drop of the solution and testing it on a white porcelain "spot plate" with a drop of potassium ferricyanide solution. This method is capable of giving excellent results after a little practice. Objection can be raised that some of the solution is lost by taking out the drops of solution for the tests, and if the testing is started too soon, the loss may be appreciable. Since a drop of 0.05 ml is only 1/4000 of a total volume of 200 ml, this error is not serious if the iron content is less than 0.1 g when the first test is made. Another difficulty lies in the fact that a negative test for Fe^{++} in a single drop of solution does not prove positively that the entire solution contains less than 0.2 mg of Fe^{++} unless the test serves to indicate 0.00005 mg of Fe^{++} in the drop taken.

[1] The dichromate solution can be made exactly tenth-normal by dissolving 4.903 g of pure $K_2Cr_2O_7$ in water, making up to exactly 1 l in a volumetric flask, and mixing well by pouring the solution back and forth from the flask to a dry beaker and back to the flask at least four times.

(2) Just as there are dyestuffs which change color at a definite pH value of an aqueous solution and serve as indicators in alkalimetry and acidimetry, so there are certain organic substances which change color as a result of oxidation or reduction Diphenylamine, $(C_6H_5)_2NH$, diphenylbenzidine $[C_6H_4\cdot NH\cdot C_6H_5]_2$, and diphenylamine sulfonic acid, $(C_6H_5)NH(C_6H_4\,SO_3H)$, are such substances. Each of these is oxidized less readily than ferrous ions. During the oxidation of Fe^{++} by $Cr_2O_7^{--}$, the Fe^{+++}/Fe^{++} oxidation potential rises as the concentration of Fe^{++} becomes smaller and that of the Fe^{+++} becomes larger, or, in other words, it becomes harder for the oxidation to take place. There is not quite enough difference between the oxidation-reduction potentials of the Fe^{+++}/Fe^{++} and that of the above-mentioned organic substances to insure that the oxidation of the Fe^{++} is complete before that of the amine starts, but this difficulty as well as the effect of yellow ferric chloride in the solution can be overcome by adding some phosphoric acid which removes Fe^{+++} and $FeCl_3$ from the solution, forming a colorless acid phosphate complex. On the other hand, it requires a measurable quantity of the dichromate solution to accomplish the oxidation of the organic compound. This causes a slight error in the opposite direction.

(3) Since the oxidation-reduction potential shown by a platinum electrode measured against a standard calomel cell changes sharply as soon as 1 drop of 0.1 N dichromate solution in excess is added, the potentiometer is capable of indicating a sharp end point in the titration of a ferrous solution with dichromate.

· Any one of the above methods can be used for determining the end point. It is important to use the same method in standardizing the solution as in the analysis because a slight excess of reagent causes a low standardization value and a high value in an analysis. A titration error, therefore, is compensated when the same error is made in the standardization and in the analysis. The compensation is exact when the same volume of reagent is used in the analysis as in the standardization.

1. Prepare a fresh solution of about 10 mg of pure potassium ferricyanide in 10 ml of distilled water. Do not attempt to use a solution that was prepared on another day. With a stirring rod, transfer small drops of this indicator solution to the cavities in a spot plate or to a paraffin coating on a white surface. When about 30 ml of the dichromate solution has been added from a buret, take out a drop of the solution on the end of a stirring rod and add it to a drop of the potassium ferricyanide solution. Wash the stirring rod before returning it to the solution. If the test shows a strong blue color, continue adding the dichromate in 1.0- to 0.25-ml portions until only a light blue test is obtained, and then test after each drop or two.

If the indicator solution has stood for some time and a little ferrocyanide is present, a good end point will not be obtained. If the indicator solution is too strong or more than a small drop is used, the test will appear green instead of blue owing to the yellow color of the reagent; and with a strong indicator solution a reddish appearance is sometimes obtained. It is best to add a series of small drops of indicator solution to the test plate and add the drops of titrated solution in regular sequence,

from a dropper until the solution is colorless,[1] but avoid adding an excess. Dilute with 150 ml of water, cool under the water faucet, and add 10 ml of mercuric chloride solution. Allow to stand about 2 minutes and titrate with dichromate, determining the end point as described on p. 576.

From the net volume of potassium dichromate solution, n ml, required to oxidize a solution of ferrous salt from p g of iron wire, compute the normality of the dichromate solution as follows:

$$\frac{p}{n \times 0.05585} = N$$

3. **Indirect Standardization against Sodium Oxalate.** Either of the above methods of standardization will give results which are sufficiently accurate for practice with the potassium dichromate titrations. If, however, it is desired to get results which will be correct within less than 0.25 per cent of the total iron content (e.g., if it is desired in the analysis of an iron ore containing 60 per cent Fe_2O_3 to get results which are within less than 0.15 per cent of this value), neither method is satisfactory. If the bottle containing the ferrous ammonium sulfate is left standing exposed to the air, and this will happen when a sample is kept in a phial under a cork stopper because cork, unless paraffined, is not impervious to air, there will be a gradual efflorescence of the crystals and as a result the iron content will become greater than the theoretical value of the pure salt. When iron wire is used as a standard, there may be some unobserved rust on the wire or there may be sufficient impurity in the metal to affect the results appreciably.

The Bureau of Standards will furnish at a reasonable price a sample of sodium oxalate which, when handled as directed, may be regarded as better than 99.99 per cent pure. The reaction between sodium oxalate and potassium dichromate cannot be used to serve as a *direct* method of standardization. In cold, dilute acid solutions,

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[1] There is usually a slight oxidation of the iron and formation of yellow ferric chloride, unless special pains are taken to exclude air during the heating and cooling.

$$4Fe^{++} + O_2 + 4H^+ \rightarrow 4Fe^{+++} + 2H_2O \qquad Fe^{+++} + 3Cl^- \rightleftharpoons FeCl_3$$
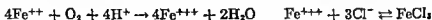
The stannous chloride reduces the ferric salt:

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

and the excess reducing agent reacts with mercuric chloride to form a precipitate of mercurous chloride: $SnCl_2 + 2HgCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$, provided that a considerable excess of mercuric chloride is added. If, however, too much stannous chloride is present, some metallic mercury is precipitated:

$$SnCl_2 + HgCl_2 \rightarrow SnCl_4 + Hg$$
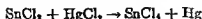
and the analysis is spoiled, because the precipitated mercury dissolves in acid when an oxidizing substance is present. The mercurous chloride precipitate should be white and silky in appearance; if it is dark colored, discard the solution.

As reagents use a solution of 50 g $SnCl_2 \cdot 2H_2O$ in 100 ml of concentrated hydrochloric acid, and a solution of 27 g mercuric chloride in a liter of water.

the oxalate ion is not oxidized quantitatively by dichromate. An indirect method, however, can be used.

Procedure. Standardize a solution of potassium permanganate against pure sodium oxalate as directed on p. 538. With the aid of a pipet, transfer 25-ml portions of a ferrous sulfate solution (see p. 576) to each of four 400-ml beakers or 300-ml Erlenmeyer flasks. Titrate two of these portions against the potassium permanganate solution which has just been standardized and the other two portions against the potassium dichromate solution. Then if a ml of N_a-normal permanganate are used and b ml of the dichromate solution, the normal concentration, N_b, of the latter is $(a/b) \cdot N_a = N_b$. Each of the above titrations should agree within 2 parts in 1000 of its duplicate, and the final results should be within 0.2 per cent of the truth.

Determination of Iron in Limonite

Weigh out accurately to four decimal places about 0.5 g of finely powdered ore into a small porcelain crucible. Using a small flame, roast the ore at dull redness for 5 minutes to destroy organic matter. Allow the crucible to cool, transfer the limonite to a small beaker, and remove the stain in the crucible by heating with four 5-ml portions of 6 N hydrochloric acid. Heat the limonite with the acid until the residue no longer shows the limonite color. Add stannous chloride dropwise to the hot solution until the yellow color due to ferric chloride disappears and the solution is nearly colorless,[1] but avoid an excess. If more than 1 drop in excess is added, add a little potassium permanganate till a yellow color is obtained and repeat the reduction. Cool, dilute to 50 ml, and quickly add 8 ml of saturated mercuric chloride solution. Wait 3 minutes to make sure that the reaction is complete, transfer to a larger beaker, dilute to about 300 ml, and titrate with dichromate without further delay.

Determination of Chromium in Chromite

By fusion with sodium peroxide, the trivalent chromium is oxidized to chromate:

$$2FeCr_2O_4 + 7Na_2O_2 \rightarrow 2NaFeO_2 + 4Na_2CrO_4 + 2Na_2O$$

[1] The addition of 3 ml of 0.5 per cent stannous chloride solution will hasten the dissolving of the limonite. It is important to avoid an excess of stannous chloride which will cause reduction of mercuric chloride to mercury and spoil the analysis. The roasting in the porcelain is unnecessary if the ore contains no organic matter. Sometimes a little Na_2CO_3 added to the ore before the roasting helps to make the sample dissolve more readily in acid.

When the melt is leached with water, the iron is precipitated as ferric hydroxide and the chromate dissolves:

$$NaFeO_2 + 2H_2O \rightarrow NaOH + Fe(OH)_3$$
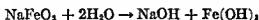
It is well to add a little more peroxide to make sure that the chromium is fully oxidized. Then the excess peroxide is decomposed by boiling the alkaline solution, the precipitate is dissolved in sulfuric acid, a known volume of standard ferrous sulfate is added, and the excess ferrous salt is titrated with dichromate.

Weigh out 0.3–0.5 g of ore into a 30–35 ml iron crucible and mix with about 4 g of sodium peroxide, using a dry stirring rod. Remove any adhering powder from the rod by stirring about 1 g of sodium peroxide with it. Cover the mixture in the crucible with this last portion of peroxide. Place the lid on the crucible, gradually heat the contents to the melting point, and maintain the fusion temperature for 5–6 minutes. Allow the melt to cool, place the crucible in a 300-ml beaker, and add 150 ml of cold water, keeping the beaker covered to avoid loss by effervescence.

When the fused mass has disintegrated, remove the crucible and wash it thoroughly. Add 0.5 g more of peroxide and gradually heat the liquid to boiling. Boil very gently for 15 minutes to make sure that all peroxide is decomposed. Allow the solution to cool somewhat, make distinctly acid to litmus, and add 10 ml of 6 N sulfuric acid in excess. Dilute to 200 ml and add, from a clean pipet, which has been rinsed three times with a little of the solution, 25 ml of standard (approximately 0.1 N) ferrous ammonium sulfate solution. Stir and test a drop of the solution on a white surface with fresh potassium ferricyanide solution. If no blue color is obtained, add another 25-ml portion of ferrous salt and continue adding it until an excess is present. Then titrate the excess with 0.1 N potassium dichromate solution.

On the same day that the analysis is made, take 25 ml of the ferrous solution, dilute to 300 ml, add 10 ml of 6 N sulfuric acid, and titrate with potassium dichromate solution. Compute the percentage of chromium present as follows:

Let a = milliliters of N-normal $K_2Cr_2O_7$ required to neutralize one pipetful of ferrous solution.

b = number of pipetfuls of ferrous solution used (p. 576).

n = milliliters of $K_2Cr_2O_7$ used in the final titration.

s = weight of sample.

e = milliequivalent weight (0.01734 g Cr; 0.02534 g Cr_2O_3; 0.03731 g $FeCr_2O_4$).

$$\frac{(a \cdot b - n)N \times e \times 100}{s} = \%$$

The analysis can be made with diphenylamine sulfonic acid as indicator. In this case it is necessary to add phosphoric acid, and proceed as described on p. 578 after adding enough ferrous salt to give a clear blue color to the solution.

C. IODIMETRY

The fundamental reaction of iodimetry is the following:

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

or

$$2S_2O_3^{--} + I_2 \rightarrow 2I^- + S_4O_6^{--}$$
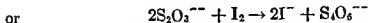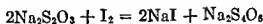
If to a solution containing a little iodine some starch solution is added, and sodium thiosulfate solution is run in from a buret, the blue color of the iodo-starch will disappear from the solution as soon as all the iodine has been reduced to iodide in accordance with the above equation. This is one of the most sensitive reactions used in analytical chemistry. If, therefore, a sodium thiosulfate solution of known strength is at hand, we have a means of determining not only iodine itself, but all those substances (oxidizing agents) which when treated with potassium iodide set iodine free, or when acted upon by hydrochloric acid evolve chlorine. Consequently, iodimetric processes are not only accurate but also capable of most general application.

Under iodimetry two kinds of methods are studied: (a) *direct methods*, in which iodine solution is used as the reagent and the end point is the blue color imparted to starch as soon as 1 drop of the reagent in excess has been added; and (b) *indirect methods*, in which an acid solution of some oxidizing agent is treated with an excess of potassium iodide and iodine equivalent to the quantity of oxidizer present is liberated   In the direct methods, iodine is used as an oxidizing agent; in the indirect methods hydriodic acid is used as a reducing agent.   Iodimetric methods have, therefore, been applied to numerous reactions of oxidation and reduction.   As a rule, these methods are sensitive and accurate.   Direct iodimetric methods are the oxidation of sulfurous acid to sulfuric acid, of hydrogen sulfide to free sulfur, of stannous chloride to stannic chloride, of arsenite to arsenate in a solution kept nearly neutral, and of trivalent antimony salt to the quinquevalent condition in a neutral solution.   Indirect methods in which iodine equivalent to the substance analyzed is liberated by adding an excess of potassium iodide to the acid solution are illustrated by the determinations of bromine, chlorine, iodate, periodate, hypobromite, bromate, hypochlorite, chlorite, chlorate, persulfate, permanganate, hydrogen peroxide, nitrite, arsenate in strongly acid solutions, ferricyanide, chromate, permanganate, manganese dioxide, lead dioxide, minium or red lead, ferric ions, cupric ions, and antimonate ions.

The words *iodimetric* and *iodometric* have been used more or less indiscriminately by chemists. Thus, of thirteen textbooks selected at random, the f

OXIDATION METHODS

as those in which iodine solution is used as oxidant and iodometric methods as those in which iodine is liberated and the final titration is made with thiosulfate. It is not at all unreasonable to make such a distinction, and perhaps in the future it will be made more generally. In this book, as the above paragraph shows, there is no attempt to make such a distinction, and the term *iodimetric* is used to cover both types of reactions In the previous edition, the other spelling was used.

The potential of the normal iodine/iodide system is $+0.535$ volt, which shows that iodine is a much weaker oxidizing agent than permanganate, ceric salt, or dichromate. Its potential does not depend upon the acidity of the solution, but the normal potentials of anions such as permanganate, dichromate, arsenate, antimonate, etc., do to a marked degree. For example, it is possible to oxidize arsenic quantitatively by iodine from the trivalent to the quinquevalent state if the pH is kept between 4 and 9, but in the presence of considerable hydrochloric acid the reduction from the quinquevalent to trivalent state takes place completely upon the addition of an excess of potassium iodide.

The end point in iodimetric processes is usually determined by the blue color of starch iodide which is formed when starch is present as soon as a very slight excess of iodine is present. In making titrations with iodine, therefore, starch can be added at the start and the approach of the end point will be shown by the formation of a dark blue color when the drop of iodine touches the solution but the color fades as the solution is stirred. At the end point, the color will not fade. In the indirect titrations, on the other hand, the starch should not be added until toward the end of the titration, when the presence of free iodine is not clearly shown by the lack of brown color.

Instead of starch, many chemists prefer to use carbon tetrachloride. One liter of pure water will dissolve only about 0.32 g of pure iodine, but the same quantity of CCl_4 will dissolve over 30 g of it. Iodine, therefore, is about 100 times as soluble in the CCl_4 as it is in water, and the CCl_4 solution is very highly colored. When CCl_4 is added to a water solution it falls to the bottom of the vessel and does not dissolve appreciably. If the water contains a little dissolved iodine, then, on shaking the greater part of the iodine will dissolve in the CCl_4, because of its greater solubility in it, and the color of the few drops of CCl_4 will be very much deeper than that of the original aqueous solution. Indirect iodimetric titrations are, therefore, often made in a 250-ml glass-stoppered bottle. After adding the excess of potassium iodide, a little carbon tetrachloride is added and the titration with sodium thiosulfate is begun. At first the presence of iodine in the aqueous solution will be apparent, and gentle rotation of the liquid causes sufficient mixing. Toward the end of the titration, the bottle is stoppered and shaken after each addition of sodium thiosulfate, and the end point is when the CCl_4 solution becomes colorless. In the distribution of a substance between two immiscible solvents, the ratio of the concentrations remains constant for a given molecular species. Therefore, as soon as some of the iodine is reduced in the aqueous layer by means of the thiosulfate, some of the iodine will pass from the CCl_4 to the water. Shaking the mixture helps to establish the equilibrium by breaking up the CCl_4 bubble and forcing it through all parts of the aqueous solution. This method is more sensitive than the determination of the end point with starch.

It was stated above that only about 0.32 g of iodine will dissolve in a liter of water. This corresponds to a normal concentration of 0.0025. In aqueous potassium iodide solution, the solubility is increased greatly; thus by adding 65 g of KI to a liter of water as much as 35 g of iodine will dissolve, which corresponds to a normal concentration of 0.275, and if 100 g of KI is present in 200 ml of water 153 g of

iodine will dissolve. In such solutions, the following reaction takes place to a considerable extent:

$$I_2 + I^- \rightarrow I_3^-$$

The reaction constant for this equilibrium has the high value of 770. The vapor pressure of the iodine from the aqueous solution is lowered by the formation of the triiodide anion, and yet the solution as a reagent behaves exactly like free iodine. To a considerable extent the potassium iodide interferes with the dissolving out of the iodine by another solvent such as CCl_4 but not enough to prevent the determination of the end point as indicated above.

The Starch Solution

Triturate 0.5 g of *soluble starch* with a little cold water to a thin paste, rinse this into 25 ml of boiling water, and boil about 2 minutes. Cool, and add 1.0 g of KI. Use 0.5 ml for each 100 ml of solution.

Sensitiveness of the Iodo-Starch Reaction

Iodine produces a blue color with starch only when hydriodic acid or a soluble iodide is present, and further, the formation of the blue color not only depends upon the presence of iodide but also is largely influenced by the concentration of the iodide solution. With the same amount of iodide and different volumes of liquid quite different amounts of iodine are necessary to produce the blue color. From this it is evident that in any iodimetric analysis about the same concentration should be maintained as in the standardization used for the analysis. When 0.1 N solutions are used, the error produced by not following this rule is a small one and for most purposes can be neglected. On the other hand, when an analysis is made with 0.01 N solutions, a large error may be introduced and a blank should always be made to determine how much iodine solution is required to give an end point. The results of a series of experiments show that the amount of iodine solution necessary to produce the blue color in the absence of potassium iodide is directly proportioned to the dilution. If the solution contains 1 g of potassium iodide, a blue color will be produced by the same amount of iodine solution as long as not more than 150 ml of solution is present, but with a greater volume than that, more iodine is necessary irrespective of whether the solution contains 1 g or more of potassium iodide.

Preparation of Sodium Thiosulfate Solution

From the equation on p. 583 it is evident that an equivalent weight of iodine, the atomic weight in grams, is equal to 1 mole of $Na_2S_2O_3$. Hence, exactly 0.1 mole of crystallized sodium thiosulfate ($Na_2S_2O_3 + 5H_2O$) is required to make 1 l of tenth-normal solution.

A solution of pure sodium thiosulfate in doubly distilled water will keep very well, but thiosulfate solutions usually deposit sulfur on standing and the titer changes until the decomposition brought about by impurities is complete. The principal cause of the decomposition is bacterial action. Sterile solutions, free from carbon dioxide, keep indefinitely. The addition of about 3.8 g of borax per liter helps to keep the solution sterile, but the solution should be filtered if turbid.

Prepare the thiosulfate solution by dissolving the required amount of the commercial salt in freshly boiled water containing a little borax. If convenient, it is well to let the solution stand a week or so before determining its exact concentration.

The molecular weight of $Na_2S_2O_3 \cdot 5H_2O$ is 248.19. To prepare 1 l of 0.1 N solution 24.82 g of the salt is necessary, or, in round numbers, 25 g.

Standardization of Sodium Thiosulfate Solution

1. *With Copper Wire*

In technical work it is customary to standardize the thiosulfate solution against pure copper. Weigh out 0.2 g of pure copper wire into a 200-ml Erlenmeyer flask and dissolve in 5 ml of 8 N HNO_3. Dilute with 25 ml of water, boil a minute to remove oxides of nitrogen, and add 1 g of urea. Remove the flask from the flame and add strong ammonia until a white precipitate begins to form; if a permanent blue color is produced, boil off the excess ammonia. Add 7 ml of glacial acetic acid or 20 ml of 6 N acetic acid, which dissolves any precipitate or copper oxide that has formed. Cool to room temperature, add 3 g of potassium iodide, and titrate the brown solution with sodium thiosulfate until nearly colorless, then add starch solution, and complete the titration. In making the titration for the first time, one is bothered somewhat by the fact that the cuprous iodide is usually colored a little by adsorbed iodo-starch and is not a pure white at the end point. If t ml of the thiosulfate solution were used in titrating a g of copper, then 1 ml of thiosulfate = a/t g Cu and the thiosulfate solution is $a/(t \times 0.06357)$ normal. The reactions that take place can be expressed as follows:

$$3Cu + 8H^+ + 2NO_3^- \rightarrow 3Cu^{++} + 4H_2O + 2NO \uparrow$$
$$HNO_2 + Br_2 + H_2O \rightarrow HNO_3 + 2HBr$$
$$Cu^{++} + 4NH_3 \rightarrow Cu(NH_3)_4^{++}$$
$$Cu(NH_3)_4^{++} + 4HC_2H_3O_2 \rightarrow Cu^{++} + 4NH_4^+ + 4C_2H_3O_2^-$$
$$2Cu^{++} + 4I^- \rightarrow Cu_2I_2 + I_2$$
$$I_2 + 2S_2O_3^{--} \rightarrow 2I^- + S_4O_6^{--}$$
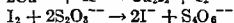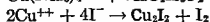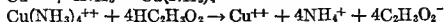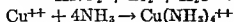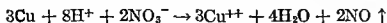
Although 4 molecules of iodide react with 2 of copper, only 1 molecule of iodine is liberated. The equivalent weight of copper, therefore,

corresponds to the reduction of *bivalent* copper to *univalent* copper and is the atomic weight of copper.

Note: The precipitate of cuprous iodide is usually colored pink at the end point because of adsorbed iodine, and this iodine slowly comes back into solution to give a fading end point. The addition of 2 g KCNS or NH$_4$CNS (dissolved in 10 ml of water) a little before the end point is reached, when the starch indicator solution is to be added, will serve to displace the iodine adsorbed on the surface of the precipitate and give a better end point. A little nitrobenzene has the same effect.

2. With Pure Iodine

Commercial iodine is contaminated with chlorine, bromine, water, and sometimes cyanogen; it must be purified. For this purpose grind 5 or 6 g of the commercial product with 2 g of potassium iodide; any chlorine or bromine present forms potassium chloride or bromide, setting free an equivalent amount of iodine. Place the mixture in a dry casserole (Fig. 86)[1] which rests in a muffle. Upon the casserole place a flask filled with cold water. Have a wire gauze at the bottom of the muffle and a Bunsen flame beneath this. The iodine sublimes rapidly and collects as a crystalline crust on the bottom of the flask, and practically none of it is lost. As soon as the evolution of violet vapors from the bottom of the casserole has practically ceased, the sublimation is complete. Remove the flame and, after

Fig. 86.

allowing to cool, take away the flask with the iodine adhering to it. To remove the iodine, pass a current of cold water through the tube *a* into the flask and out at *b*. This causes the glass to contract somewhat and the whole of the iodine crust can be removed by lightly scraping with a clean glass rod. Catch it upon a watch glass, break it up into large pieces, and repeat the sublimation without the addition of potassium iodide at as low a temperature as possible; in this way a product free from potassium iodide is obtained. Grind the iodine somewhat in an agate mortar and dry in a desiccator containing calcium chloride. If dried over sulfuric acid, some of the acid is
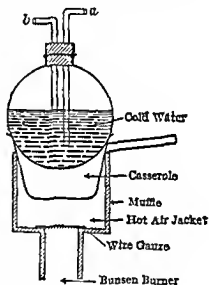
[1] C. R. McCrosky, *J. Am. Chem. Soc.*, **40**, 1664 (1918).

likely to be present in the iodine. Furthermore, the cover of the desiccator must not be greased, for grease is attacked by iodine vapors, forming hydriodic acid, which might cause contamination.

Weighing out the Iodine. In each of 2 or 3 small weighing tubes with tightly fitting glass stoppers place 2-2.5 g of pure potassium iodide free from iodate and 0.5 ml of water (not more); stopper the tubes and weigh accurately. Then open the tubes and add 0.4-0.5 g of pure iodine to each. Quickly insert the stopper and again weigh; the difference shows the amount of iodine. As the tubes are cooled by the dissolving of the iodine, moisture sometimes collects on the outside and must be wiped off before weighing. The iodine dissolves almost instantly in the concentrated potassium iodide solution. Place one of the tubes in the neck of a 500-ml Erlenmeyer flask which is held in an inclined position and contains 200 ml of water and about 1 g of potassium iodide. Drop the tube to the bottom of the flask, but just as it begins to fall remove the stopper and allow it to follow. In this way no iodine is lost, which is likely to happen if the contents of a tube are washed into the water. A solution is thus prepared containing a known amount of iodine. To it add the sodium thiosulfate solution to be standardized from a buret until the liquid is pale yellow. Then add 2 or 3 ml of starch solution and carefully titrate until colorless. From the mean of two or three determinations, the strength of the thiosulfate solution is calculated.

If the weight of iodine equivalent to 1 ml of sodium thiosulfate solution is divided by 0.1269 (the milliequivalent of iodine), the *normality* of the solution will be obtained.

3. *With Potassium Permanganate (Volhard)*

On adding potassium permanganate to an acid solution containing potassium iodide, the following reaction takes place:

$$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{++} + 8H_2O + 5I_2$$
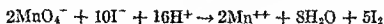
The reaction is quantitative if the correct conditions are maintained.

Measure out 25-40 ml of standardized tenth-normal permanganate solution from a pipet or buret into a 300-ml Erlenmeyer flask containing 3 g of potassium iodide, 50 ml of water, and 5 ml of concentrated hydrochloric acid. Let stand in the dark for 3 minutes, dilute to 200 ml, and titrate slowly with the thiosulfate solution, adding 2 ml of starch indicator solution toward the last.

4. *With Potassium Dichromate*

The reaction between potassium dichromate and potassium iodide can also be used for the standardization of sodium thiosulfate solutions;

tbe dichromate is reduced to green cbromic salt and an equivalent weight of iodine being set free provided that the solution is 0.2-0.4 N in acid.

$$Cr_2O_7^{--} + 6I^- + 14H^+ \rightarrow 2Cr^{+++} + 3I_2 + 7H_2O$$
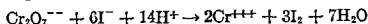
Prepare tenth-normal potassium dichromate solution by dissolving 4.903 g of the pure, dry salt in water and diluting to 1 l at 20° in a measuring flask. Mix well by pouring back and forth from the flask to a beaker at least 4 times. Measure out 20-40 ml of the dichromate solution, with a pipet or buret, into a 500-ml beaker containing 50 ml of water, 10 ml of concentrated bydrocbloric acid, and 3 g of potassium iodide. Allow the reaction to proceed in the dark for 5 minutes, then dilute to 400 ml and titrate with tentb-normal thiosulfate solution, adding starch toward the last.

5. With Potassium Biiodate (C. Than)[1]

If a solution of potassium biiodate is added to a solution of potassium iodide containing hydrochloric acid, the following reaction takes place:

$$\underset{389.95}{KIO_3 \cdot HIO_3} + 10KI + 11HCl = 11KCl + 6H_2O + \underset{1523}{6I_2}$$
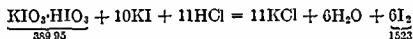
If, therefore, 3.250 g of pure potassium biiodate is contained in 1 l of the aqueous solution, 10 ml of such a solution on being treated with an excess of potassium iodide and hydrochloric acid will set free exactly as much iodine as would be contained in 10 ml of 0.1 N iodine solution. By means of such a solution a known amount of iodine may be obtained at any time and in tbis way the solution of sodium thiosulfate may be standardized. At present it is possible to obtain commercially very pure potassium biiodate, but it is best to prepare a solution by weighing out 3.250 g per liter and determine the concentration accurately by titrating it against a solution of thiosulfate which has been freshly standardized against pure iodine. In this way a solution is obtained which can be conveniently used from time to time for testing the concentration of the thiosulfate solution.

Method of Titrating. Place 1-2 g of pure potassium iodide in a beaker, dissolve in as little water as possible, and to this add 5 ml of 6 N hydrochloric acid, and then 20-25 ml of the biiodate solution (never in the reverse order). Iodine is liberated, immediately and quantitatively. Dilute with 200 ml of distilled water, and titrate the iodine as under 1.

Remark. Instead of a solution of potassium biiodate, solid potassium iodate or potassium bromate can be used. One mole of each of these last two salts liberates 3 moles of I_2 when treated with potassium iodide and dilute acid.

[1] Z. anal. Chem., 16, 477 (1877).

Preparation of Tenth-Normal Iodine Solution

No advantage is obtained by dissolving the desired quantity of sublimed iodine in a definite volume of solution, for the latter cannot be kept very long unchanged. It is more practical to prepare the iodine solution by placing 20–25 g of pure potassium iodide in a liter bottle, dissolving it in as little water as possible, and then adding about 12.7 g of commercial iodine, weighed out roughly on a watch glass. Shake the contents of the flask until all the iodine is dissolved. When this is accomplished, dilute the solution to about 1 l and standardize according to one of the following methods. The solution should be used in a glass-stoppered buret.

Standardization of Iodine Solution

1. *With 0.1 N Sodium Thiosulfate Solution*

Take 25 ml of the well-mixed iodine solution in a 250-ml Erlenmeyer flask, dilute to 100 ml and introduce 0.1 N $Na_2S_2O_3$ solution until nearly all the iodine has reacted as shown by the color. Add 1 ml of starch paste and titrate slowly until colorless.

Remarks. To titrate a solution of iodine obtained from a solution of iodide-iodate mixture, titrate in the same way but in the presence of 20 millimoles of free hydrochloric acid.

2. *With Arsenious Acid*

If iodine is allowed to act upon a neutral solution of arsenious acid the reaction which takes place may be expressed as follows:

$$H_2AsO_3^- + I_2 + 2HCO_3^- = H_2AsO_4^- + 2I^- + H_2O + 2CO_2$$

It is necessary to keep the solution neutral or the opposite reaction will take place:

$$H_2AsO_4^- + 2I^- + 6H^+ = As^{+++} + I_2 + 4H_2O$$
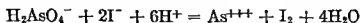
In a neutral solution arsenite can be oxidized quantitatively by means of free iodine, but in strongly acid solution arsenic acid can be reduced quantitatively to the trivalent condition by means of iodide (cf. p. 584). To accomplish a complete oxidation of the arsenic by iodine, the solution must be kept approximately neutral to phenolphthalein. This is usually accomplished by providing an excess of sodium bicarbonate, by adding normal sodium carbonate to the cold acid solution, or by adding some disodium phosphate. Caustic alkali cannot be used because it

reacts with iodine to form hypoiodite and iodide. A little neutral sodium carbonate does no harm if added to an acid solution because the liberated carbon dioxide neutralizes the hydroxyl ion formed by hydrolysis of the carbonate.

From the above equation, and the fact that the valence change of arsenic is 2, it follows that the equivalent weight of arsenic is one-half the atomic weight. Ordinarily, the arsenite solution is prepared by weighing out pure As_2O_3. As the molecule contains 2 atoms of arsenic, it is evident that one-fourth the molecular weight in grams is the equivalent weight of As_2O_3.

To prepare 0.1 N arsenious acid solution, dissolve 4.946 g of the pure sublimed oxide and 15 g of sodium carbonate by warming with 150 ml of water. Transfer the solution to a liter measuring flask, add 25 ml of normal acid, and dilute at 20° to the mark.

To prepare pure arsenious oxide from the commercial product, sublime by heating in a porcelain dish and collect the sublimate on a watch glass. If a yellow sublimate of sulfide is noticed, dissolve the sample in hot 4 N hydrochloric acid, filter off the undissolved sulfide, and cool the filtrate to cause crystals to deposit. Filter, wash with water, and then sublime. Dry over calcium chloride in a desiccator.

Titrate the arsenite against the iodine solution in the usual way. Deiss,[1] however, finds that iodine gradually changes to iodate on standing and the iodate does not react with arsenic in the presence of sodium bicarbonate. He proceeds as follows:

Add 25 ml of the iodine solution to 200 ml of water. Add 2 ml of 6 N hydrochloric acid and then 2 g of sodium bicarbonate. As soon as it has dissolved titrate with sodium arsenite.

A solution of sodium arsenite gradually oxidizes on long standing.[2]

3. With Anhydrous Sodium Thiosulfate[3]

Anhydrous sodium thiosulfate may be prepared in a state of sufficient purity to permit its use for standardizing iodine solutions. Prepare a saturated filtered solution of the commercial salt at 30° to 35° and then cool while stirring constantly. Collect the salt that deposits; dry over sulfuric acid until it falls to a powder and a little of it in a test tube shows no sign of fusion when heated to 50°. Effect the final dehydration by heating at 80° with repeated stirring of the powder.

[1] *Chem. Ztg.*, **38**, 413.

[2] S. W. Young, *J. Am. Chem. Soc.*, **26**, 1028 (1904).

[3] F. A. Gooch and F. H. Heath, *Am. J. Sci.*, [4], **24**, 68 (1907); F. H. Heath, *ibid.*, [4], **25**, 513 (1908).

Young standardized a solution of iodine by this method and obtained the same value as by titrating against a thiosulfate solution which had been standardized against pure iodine.

Analyses by Iodimetric Methods

1. Determination of Free Iodine

1000 ml of 0.1 N thiosulfate solution = 12.69 g I

Dissolve the iodine in a solution of potassium iodide and titrate either with sodium thiosulfate or with arsenious acid exactly as described under the standardization of an iodine solution.

2. Determination of Chlorine in Chlorine Water

1000 ml of 0.1 N thiosulfate solution = 3.546 g Cl

Add a measured amount of chlorine water to a solution containing an excess of potassium iodide. Hold the point of the pipet just above the surface of the iodide solution contained in a glass-stoppered bottle. After the chlorine water has been added, stopper the bottle, vigorously shake the contents, and titrate the liberated iodine with sodium thiosulfate as above:

$$2KI + Cl_2 = 2KCl + I_2$$
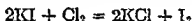
3. Determination of Bromine in Bromine Water

1000 ml of 0.1 N thiosulfate solution = 7.992 g Br

The procedure is the same as under 2:

$$2KI + Br_2 = 2KBr + I_2$$
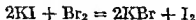
4. Determination of Hypochlorous Acid in the Presence of Chlorine

The determination is based upon the following reactions:

$$HOCl + 2KI = KCl + KOH + I_2$$
$$Cl_2 + 2KI = 2KCl + I_2$$
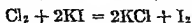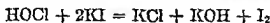
One mole of hypochlorous acid liberates 1 mole of iodine but produces at the same time 1 mole of potassium hydroxide, while the chlorine simply sets free an equivalent amount of iodine. After neutralizing the alkali by means of an excess of hydrochloric acid and determining the iodine by titration with sodium thiosulfate, the excess of hydrochloric acid is titrated with standard alkali solution.

Procedure.   Add a measured excess of 0.1 N hydrochloric acid to a potassium iodide solution, and to this add a known amount of the solution containing chlorine and hypochlorous acid.   Titrate the iodine set free with 0.1 N thiosulfate solution.   Then add methyl orange to the colorless solution and titrate the excess of hydrochloric acid with 0.1 N NaOH.   The alkali hydroxide produced by the action of the hypochlorous acid upon the iodide requires half as much 0.1 N acid for neutralization as is required of 0.1 N $Na_2S_2O_3$ solution to react with the iodine set free by the action of the hypochlorous acid.

Example.   If V ml of chlorine + hypochlorous acid solution was taken for analysis, t ml 0.1 N HCl was added at the start, T ml 0.1 N $Na_2S_2O_3$ used for titrating the iodine, and t_1 ml 0 1 N NaOH for titrating the excess of acid, then $t - t_1$ ml of 0.1 N acid was required to neutralize the alkali hydroxide and $2 (t - t_1)$ ml of 0.1 N $Na_2S_2O_3$ to react with the iodine formed from the hypochlorite.

Hence $(t - t_1)$ 0.005247 [1] = g HOCl in V ml solution, and

$$T - 2 (t - t_1)\ 0\ 003546 = \text{grams Cl in } V \text{ ml solution}$$

5. Determination of Iodine in Soluble Iodides[2]

(a) By Decomposition with Ferric Salts

If a solution of a soluble iodide is treated with an excess of ferric-ammonium alum and acidified with sulfuric acid, the ferric salt will be reduced to ferrous salt with separation of iodine:

$$Fe_2(SO_4)_3 + 2HI = H_2SO_4 + 2FeSO_4 + I_2$$
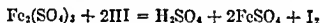
If the solution is heated to boiling, the iodine escapes with the steam and can be collected in a solution of potassium iodide and then titrated with sodium thiosulfate or arsenious acid.   This method is suited for separating iodine from bromine, for bromides do not reduce ferric salts.   The bromide will be found in the residue obtained after the distillation, and is best determined gravimetrically.

(b) By Decomposition with Nitrous Acid (Fresenius)

This excellent method, which is especially suited for determining small amounts of iodide in the presence of bromide and chloride in mineral waters, depends upon the

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[1] HOCl = 52.47; 1 ml 0 1 N solution = 0 005217 g HOCl (against NaOH).

[2] In the case of insoluble iodides, the metal must first be removed if the iodine is to be determined volumetrically.   This can be accomplished by the method of Mensel (Z. anal. Chem., 12, 137).   It may be said, however, that the volumetric method offers no advantages over the gravimetric one.

easy oxidation of hydriodic acid by means of nitrous acid:

$$2HI + 2HNO_2 = 2H_2O + 2NO + I_2$$
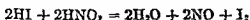
Hydrochloric and hydrobromic acids are not attacked by nitrous acid.

Procedure. To the small apparatus shown in Fig. 87 transfer the neutral or slightly alkaline solution of the iodide; make slightly acid with dilute sulfuric acid, and add a little freshly distilled, colorless car-

bon disulfide (carbon tetrachloride or chloroform), so that it does not quite reach to the stopcock, near the bottom of the tube. Then introduce 2, or at the most 3, drops of "nitrose,"[1] stopper the tube, shake vigorously, and then allow the carbon disulfide to settle once more. The small amount which at first adheres to the glass sides can be made to fall to the bottom by revolving and inclining the tube. On the upper surface of the liquid there will still remain a few tiny drops of carbon disulfide. To obtain these, moisten a filter with water and place the funnel under the glass stopcock, remove the stopper from the tube, and allow the aqueous solution to run through the filter; the carbon disulfide will remain behind on the paper. Shake the carbon disulfide remaining in the tube 3 times with successive portions of distilled water, and each time allow the water to run off through the same filter. Then place the funnel at the top of the tube, puncture the filter with a pointed glass rod, and wash the carbon disulfide into the tube by means of about 0.5 ml of water. After this add 1 or 2 drops of sodium bicarbonate solution and thoroughly shake with the carbon disulfide, then add standard sodium thiosulfate solution until the reddish violet carbon disulfide solution becomes colorless.
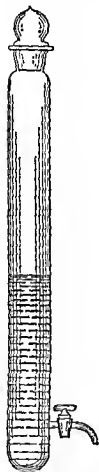
Fig. 87.

The value of the sodium thiosulfate solution is not determined as ordinarily, but by means of a potassium iodide solution treated as above described.

Remark. This method is useful for determining small amounts of iodide in the presence of relatively large amounts of chloride and bromide, as in the analysis of mineral waters. For the standardization of the sodium thiosulfate solution, as nearly as possible the same amount of

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[1] Cf. Vol. I.

potassium iodide should be used as is present in the unknown solution; this is determined by the color of the carbon disulfide. Pure potassium iodide must be used for this purpose, and its purity tested by means of a gravimetric determination of the iodine present in the salt after it has been dried at 170–180°.

The reason the sodium thiosulfate solution must be standardized in this way is as follows:

When an aqueous solution containing iodine is shaken with carbon disulfide, not all the iodine but the greater part of it will pass into the solvent. The error is compensated, however, by standardizing the solution in the same way.

If the solution of a substance is shaken with another solvent in which the former does not mix, the original amount of the substance divides itself between the two solvents, and in fact the concentration of one solution (amount of the dissolved substance present per milliliter) always bears a constant relation to that of the other.

Thus if x_0 g of iodine is dissolved in V ml of water, and the solution is shaken with V_1 ml of carbon disulfide, then x_1 g of iodine will remain in the aqueous solution and $x_0 - x_1$ g will pass into the carbon disulfide.

The amount x_1 is found by the following equation:

$$(1) \quad \frac{x_1}{V} = \frac{x_0 - x_1}{V_1} k \quad \text{and} \quad x_1 = x_0 \frac{kV}{V_1 + Vk}$$

$\frac{x_1}{V}$ and $\frac{x_0 - x_1}{V_1}$ are the concentrations in each of the solutions, and k is the distribution coefficient, which is $\frac{1}{400}$ for iodine.[1] If the aqueous solution is now shaken with the same amount of fresh carbon disulfide, then x_2 g of iodine will remain in the water and $x_1 - x_2$ will be extracted by the carbon disulfide. In this case, however,

$$(2) \quad x_2 = x_0 \left(\frac{kV}{V_1 + Vk} \right)^2 \text{ g iodine}$$

so that, after shaking n times with fresh portions of carbon disulfide, the amount of iodine remaining in the water would be:

$$(3) \quad x_n = x_0 \left(\frac{kV}{V_1 + kV} \right)^n \text{ g iodine}$$

[1] Berthelot and Jungfleisch, *Compt. rend.*, **69**, 333.

Assuming that in the analysis 0.005 g of iodine was dissolved in 10 ml of water and that this solution was shaken once with 1 ml of carbon disulfide, then according to equation (1)

$$x_1 = 0.005 \frac{\frac{1}{400} \times 10}{1 + \frac{10}{400}} = 0.005 \cdot \frac{1}{41} = 0.0001 \text{ g iodine}$$

would remain dissolved in the water, or an amount that can be neglected. The distribution coefficient, as used above, holds when the same molecular species is present in each solvent. When potassium iodide is added to the aqueous solution, KI_3 is formed and it is much harder to dissolve out the iodine. As some potassium iodide is present, the above calculation is inexact.

If, after shaking with carbon disulfide, the aqueous solution still appears yellow, it must be treated a second, and perhaps a third, time with fresh amounts of carbon bisulfide.

6. Determination of Bromine in Soluble Bromides (Bunsen)

If chlorine water is added to a colorless bromide solution in a porcelain dish, the solution becomes yellow:

$$2KBr + Cl_2 = 2KCl + Br_2$$
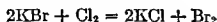
If it is heated to boiling, the bromine is expelled and the solution becomes colorless again. The addition of the chlorine water is continued until finally no yellow coloration is produced.

Preparation and Standardization of the Chlorine Water

Dilute 100 ml of a saturated chlorine water to 500 ml and titrate against a weighed amount of pure potassium bromide which has been dried at 170°, taking about the same amount of bromide for the standardization as is supposed to be present in the solution to be analyzed. During the titration, wrap the buret containing the chlorine water in black paper to protect its contents from the light, and hold the tip of the buret just above the surface of the hot bromide solution, so that as little chlorine as possible is lost by evaporation.

7. Determination of Iodine and Bromine in Mineral Waters

According to the amount of halogen present, take 5–60 l of water for the analysis. The amount of bromide and iodide present is usually small compared with the chloride, so that the residue obtained by the evaporation of a large amount of water cannot be used directly for the analysis, but by partial crystallization a mother liquor rich in bromide and iodide must first be obtained.

Procedure. Pour the water into a large evaporating dish, a liter at a time, and if not already alkaline,[1] add enough pure sodium carbonate solution to make it distinctly so, and evaporate to about one-fourth of its original volume. This causes the separation of some calcium and magnesium carbonates, as well as hydroxides of iron and manganese, but all the halides remain in solution. Filter off the residue and thoroughly wash with water. Concentrate the filtrate further until salts begin to crystallize out, and pour the hot solution into 3 times its volume of absolute alcohol; this causes the greater part of the sodium chloride and other undesired salts to precipitate. After standing 12 hours, filter the alcoholic liquid and wash the residue 5 or 6 times with 95 per cent alcohol.

To the alcoholic solution, which contains all the iodide and bromide with considerable chloride in the form of the alkali salts, add 5 drops of concentrated potassium hydroxide solution and distil off most of the alcohol, while passing a current of air through the solution by means of a capillary tube reaching to the bottom of the liquid in the distilling flask.

Evaporate the residue from the distillation until salts again begin to crystallize out and repeat the precipitation with alcohol. Again distil off the alcohol, but this time with the addition of only 1 or 2 drops of potassium hydroxide solution. According to the amount of salts present in solution repeat this operation 3 to 6 times. Place the final filtrate, after the alcohol has been distilled off, in a platinum dish, evaporate to dryness, cover the dish with a watch glass, and gently ignite the residue to destroy organic matter. Dissolve the residue from the ignition in a little water, filter off the carbonaceous material,[2] make the solution slightly acid with dilute sulfuric acid, titrate the iodine liberated by the addition of 1 or 2 drops of "nitrose," and with sodium thiosulfate, after shaking with chloroform, as described on p. 594.[3] Determine bromide in the aqueous solution obtained after the extraction of the iodine with chloroform. Make the acid solution

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[1] The solution is alkaline if after the addition of phenolphthalein the solution turns red on boiling.

[2] If the filtrate is not completely colorless, evaporate and again ignite.

[3] Lecco determines the iodine colorimetrically (Z. anal. Chem., 35, 318).

alkaline by the addition of sodium carbonate solution, add 2 drops of a saturated sugar solution, and evaporate the solution to dryness in a platinum dish. With a watch glass upon the dish, gently ignite the residue to destroy the sugar and the excess of nitrite.[1] After this has been accomplished dissolve the residue in water, filter, make slightly acid with sulfuric acid, and titrate the bromine with chlorine water as described on p. 596.

Remark. If sufficient mineral water is available it is better to divide the mother liquor containing the bromide and iodide into two portions; in one portion determine the iodine as above, and in the other determine bromine and iodine by titration with chlorine water.[2]
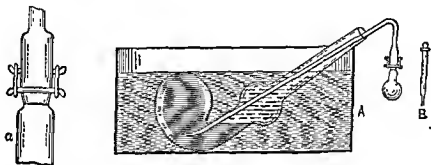
Fig. 88.

8. Analysis of Peroxides (Bunsen)

All peroxides of the heavy metals which evolve chlorine on treatment with hydrochloric acid can be determined with great accuracy by conducting the chlorine into potassium iodide solution and titrating the liberated iodine with sodium thiosulfate or arsenious acid solution. It is only necessary to make sure that the chlorine is allowed to act upon the potassium iodide without loss. For all such determinations, Bunsen employed the apparatus shown in Fig. 88. The small decomposition flask of about 40-ml capacity has ground-glass connection with the delivery tube[3] and is held firmly in place by means of rubber rings, as at a. The lower end of the bent delivery tube is drawn out into a not-too-small capillary.

Procedure. Place the finely powdered substance in the small glass-stoppered weighing tube (Fig. 88), which has a small piece of glass fused on the end, and weigh. Take hold of the tube by the glass at the

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[1] The addition of the sugar causes the nitrite to be destroyed at a lower temperature than would otherwise be the case, and the danger of losing bromine by volatilization is avoided.

[2] As the chlorine water was standardized against bromide, an amount of the bromine equivalent to the iodine present should be deducted from the amount represented by the chlorine water used; the difference shows the bromine present.

[3] Instead of the ground-glass connection, Bunsen used a tube of the same size as the neck of the flask and connected them with rubber tubing, the two glass tubes being against each other.

bottom,[1] introduce it into the neck of an absolutely dry decomposition flask, and allow the required amount of the substance to fall into it by carefully revolving the weighing tube. Again weigh the tube, to determine the amount of substance taken. Add hydrochloric acid (its concentration depends upon the nature of the substance), at once connect the delivery tubing with the flask, and introduce it into the retort containing potassium iodide solution. By means of a tiny flame, heat the contents of the flask to boiling and distil half to two-thirds of the liquid over into the retort. To prevent the iodide solution from sucking back into the flask, take out the delivery tube from the retort before removing the flame, and wash the contents of the tube into the retort:

Pour the potassium iodide solution into a large beaker, rinse out the retort several times with a little water, and then with potassium iodide solution to remove any iodine which may remain adhering to the glass. Titrate with 0.1 N sodium thiosulfate solution in the presence of starch as indicator. In this way pyrolusite, chromates, lead peroxide, minium, ceric oxide, selenic, telluric, and molybdic acids may be analyzed.

(a) Determination of Manganese Dioxide in Pyrolusite

$$1000 \text{ ml of } 0.1 \ N \ Na_2S_2O_3 \text{ solution} = \frac{MnO_2}{20} = 4.347 \text{ g } MnO_2$$

Weigh out about 0.2 g of the substance which has been dried at 120°. To this add 25 ml of 4 N hydrochloric acid and carry out the analysis as described above with 30 ml of 2 per cent potassium iodide solution in the retort:

$$MnO_2 + 4HCl = 2H_2O + MnCl_2 + Cl_2$$
$$Cl_2 + 2KI = 2KCl + I_2$$
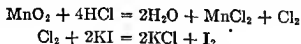
If t ml of 0.1 N $Na_2S_2O_3$ were used in titrating a g of MnO_2, then

$$\frac{0.4347 \ t}{a} = \text{per cent } MnO_2$$

The determination of chromates, lead peroxide, and selenic acid is carried out in the same way, except that 12 N hydrochloric acid is used for the decomposition.

Instead of the apparatus shown on p. 598, Rupp[2] uses a 50-ml distilling flask for the decomposition and 750-ml bottle as receiver; the bottle contains 250 ml

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[1] By holding the tube in this way, deviations of weight, due to unequal warming, are avoided.

[2] *Chem.-Ztg.*, **52**, 429 (1928).

of 1 per cent potassium iodide solution. The arm of the distilling flask is fused to 18–20 cm of tubing with about 3-mm inside diameter, and this long arm is bent downward so that the interior angle is about 135° and the tube will easily reach the bottom of the receiving bottle. The long arm is inserted in one hole of a twice-bored rubber stopper that fits the receiver. The other hole of the stopper is fitted with a tube containing glass beads and some glass wool. The top of the distilling flask carries a stopper enclosing a tube which reaches to the bottom of the flask with a 1-mm opening at the bottom. The top of this tube is closed with a pinchcock on rubber tubing, 0.2 g of the pyrolusite is introduced into the distilling flask, care being taken not to get any powder on the sides. Twenty-five milliliters of concentrated hydrochloric acid is introduced and the stopper inserted quickly. The acid is heated with a small flame, protected from drafts, until the volume is reduced one-half. Then the pinchcock is opened to prevent the liquid sucking back, the flame is removed, and the contents of the receiver are titrated with thiosulfate. It is well to put a few crystals of potassium iodide on top of the glass wool in the drying tube. Then, if this is moistened, it will show if any iodine is lost by volatilization.

(b) Determination of Telluric Acid

If the telluric acid is present as the hydrous acid ($H_2TeO_4 + 2H_2O$) or as tellurate, the analysis is performed in the same way as with selenic and chromic acids. If, however, the tellurium is present as the anhydrous acid or as the anhydride, the method must be modified, for these substances are scarcely attacked by concentrated hydrochloric acid. They are placed in the decomposition flask and dissolved in a little concentrated potassium hydroxide;[1] to the tellurate solution thus obtained the concentrated hydrochloric acid is added, and the reduction then is accomplished without difficulty:

$$K_2TeO_4 + 4HCl = 2KCl + H_2TeO_3 + H_2O + Cl_2$$
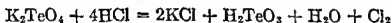
According to this equation, 1 l of 0.1 N $Na_2S_2O_3$ = 6.375 g Te = 7.975 g TeO_2.

(c) Determination of Ceric Oxide

$$1000 \text{ ml of } 0.1 \text{ } N \text{ iodine solution} = \frac{CeO_2}{10} = 17.225 \text{ g } CeO_2$$

Ceric oxide when mixed with considerable lanthanum and didymium oxides is reduced by distillation with concentrated hydrochloric acid:
$$2CeO_2 + 8HCl = 4H_2O + 2CeCl_3 + Cl_2$$

If, however, the mixture contains but little of the two last substances, or if it is pure ceric oxide, the heating with concentrated hydrochloric acid is of no avail; the ceric oxide will not dissolve.

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[1] The solution could not be effected by using *sodium* hydroxide.

In the presence of hydriodic acid, however, the reduction takes place readily, so that it is only necessary to add 2 g of potassium iodide to a weighed amount of the substance (0.67–0.68 g) in the decomposition flask, and then, after the addition of hydrochloric acid, violet vapors of iodine can be distilled from the solution:

$$2CeO_2 + 2KI + 8HCl = 2KCl + 2CeCl_3 + 4H_2O + I_2$$
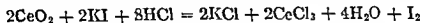
Often so much iodine will be given off that the solid is likely to stop up the tube and the flask may explode. To prevent this, do not draw out the end of the delivery tube into a capillary, but at the bottom leave an opening about 4 mm in diameter. During the operation, the flame must be protected from air currents, for otherwise there is danger of liquid sucking back from the retort.

9. Analysis of Chlorates

$$1 \text{ l of } 0.1 \text{ N Na}_2S_2O_3 = \frac{KClO_3}{60} = 2.013 \text{ g KClO}_3$$

This is carried out the same way as the analysis of pyrolusite (cf. p. 599): $KClO_3 + 6HCl = KCl + 3H_2O + 3Cl_2$.

Many oxidizing agents can be determined iodimetrically without previous distillation with hydrochloric acid.

For other methods of analyzing chlorates iodimetrically, consult H. Dietz, *Chem.-Ztg.*, 1901, 727, and Luther and Rutter, *Z. anal. Chem.*, 46, 521 (1907).

10. Determination of Hypochlorous Acid

This determination is used in the analysis of chloride of lime.

Procedure. Into a tared weighing tube introduce about 5 g of " chloride of lime," and weigh the stoppered tube. Wash into a porcelain dish, rub to a paste with a pestle, and transfer without loss to a 500-ml measuring flask. Dilute to the mark with water, and mix well. Of this turbid solution, pipet off 50 ml of the suspension into a 250-ml Erlenmeyer flask. Add 2 g of potassium iodide and 15 ml of 4 N sulfuric acid and titrate the liberated iodine with 0.1 N Na$_2$S$_2$O$_3$. Express the result in percentage of *available chlorine* which is the equivalent of the iodine titrated.

Remark. Moist samples of bleaching powder decompose into chlorite and chlorate with loss of chlorine gas. **According to the above directions, the chlorite will liberate iodine from the iodide but the chlorate will not.**

11. The Analysis of Iodates

$$1 \text{ l of } 0.1 \ N \ Na_2S_2O_3 = \frac{HIO_3}{60} = 2.932 \text{ g HIO}_3$$

Allow the solution of the iodate to run into an acid solution containing an excess of potassium iodide. Iodine is set free according to the equation: $KIO_3 + 5KI + 6HCl = 6KCl + 3H_2O + 3I_2$. Titrate the iodine with thiosulfate solution as described on p. 589.

12. The Analysis of Periodates

$$1 \text{ l of } 0.1 \ N \ Na_2S_2O_3 = \frac{HIO_4}{80} = 2.399 \text{ g HIO}_4$$

The analysis of periodates is carried out exactly as with iodates; the reaction that takes place is

$$KIO_4 + 7KI + 8HCl = 8KCl + 4H_2O + 4I_2$$
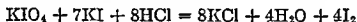
13. Analysis of a Mixture of Iodate and Periodate[1]

If a neutral or slightly alkaline solution of an alkali periodate is treated with a solution of potassium iodide, the following reaction takes place:

$$KIO_4 + 2KI + H_2O = 2KOH + KIO_3 + I_2$$

The liberated iodine is titrated with tenth-normal arsenious acid (not with sodium thiosulfate); in a neutral solution the *iodate* does not react with potassium iodide. For the analysis of a mixture of iodate and periodate, the following procedure is used:

In one sample determine the iodate + periodate by adding the solution of the substance to an acid solution containing an excess of potassium iodide and titrate the liberated iodine with sodium thiosulfate solution.

Dissolve a second sample in water, add a drop of phenolphthalein indicator, and make the solution alkaline enough to give the pink color with phenolphthalein, adding alkali if the solution is acid and hydrochloric acid if the solution is strongly alkaline. To the barely alkaline solution, add 10 ml of a cold, saturated solution of sodium bicarbonate and then an excess of potassium iodide; titrate the liberated iodine at once with 0.1 N arsenious acid.[2]

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[1] E. Müller and O. Friedberger, *Ber.*, 1902, 2655.

[2] The iodine cannot be titrated in the alkaline solution with sodium thiosulfate, and the iodine in the acid solution cannot be titrated with the arsenious acid.

Example. In a mixture of KIO_3 and KIO_4 weighing a g, the iodine liberated on treatment with an excess of KI reacts with T ml of 0.1 N $Na_2S_2O_3$ and the same weight of sample liberates in alkaline solution only enough iodine to react with t ml of 0.1 N As_2O_3 solution. By comparing the equations given under 12 and 13, it is evident that the periodate alone would react with $4t$ ml of 0.1 N $Na_2S_2O_3$ in acid solution. The amount of KIO_4 and KIO_3 present will be

$$t \times 0.01150 \text{ g or } \frac{t \times 1.150}{a} \text{ per cent } KIO_4$$

$$(T - 4t) \times 0.003567 \text{ g or } \frac{(T - 4t) \times 0.3567}{a} \text{ per cent } KIO_3$$

14. Analysis of Iodides

(a) Method of H. Dietz and B. M. Margosches[1]

$$1 \text{ l of 0.1 } N \text{ } KIO_3 = \frac{5I}{60} = 10.58 \text{ g iodine}$$

Treat the solution of the iodide with an excess of 0.1 N potassium iodate solution, make acid with sulfuric acid, add a piece of calcite as suggested by Prince,[2] and boil until all the iodine is expelled. Allow the solution to cool, then add an excess of potassium iodide, and titrate the iodine now liberated, which corresponds to the excess of potassium iodate used, with 0.1 N $Na_2S_2O_3$ solution.

From the equation

$$KIO_3 + 5KI + 6HCl = 6KCl + 3H_2O + 3I_2$$
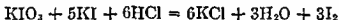
it is evident that five-sixths of the iodine liberated comes from the iodide. If, therefore, T ml of 0.1 N KIO_3 solution was added and t ml of 0.1 N $Na_2S_2O_3$ was used for titrating the excess of KIO_3, then there is present

$$(T - t) \times 0.01058 \text{ g iodine as iodide}$$

(b) Oxidation of Iodide to Iodate and Iodimetric Titration

In neutral or slightly acidic solutions, iodide can be oxidized completely to iodate by chlorine or bromine. The iodate ion formed can then be made to react with added iodide, and six atoms of iodine will be liberated for each molecule of alkali iodide originally present. The equivalent weight of I^-, in this particular case, is only one-sixth of the atomic weight. Small quantities of iodide, therefore, can be determined very satisfactorily. The excess bromine or chlorine can be removed by boiling, or, as is often more advantageous, by adding phenol or aniline. Phenol solution is often used and reacts to form mono-, di-, or tri-substitution products. The following procedure has been recommended for determining the iodide content of table salt. The so-called *iodized salt* is likely to contain about 0.02 per cent potassium iodide.

[1] *Chem.-Ztg.*, 1904, II, 1191.
[2] Inaug. Dissert., Zürich, 1910.

Procedure. Weigh out 5 g of the salt to the nearest centigram into a 250-ml Erlenmeyer flask. Add methyl orange indicator, and then carefully add 2 N H_2SO_4 till the solution is acid to the indicator and contains 2.0 ml in excess. Add small portions of freshly prepared bromine water, with gentle swirling, until the solution shows that an excess of bromine is present by assuming a permanent yellow tint. Add a few glass beads to prevent bumping, boil gently until the yellow color of the solution disappears, and continue boiling for 2 minutes more. Cool to at least room temperature, add 0.2 g KI and 2–3 ml of starch solution, mix, and titrate the liberated iodine with 0.01 N $Na_2S_2O_3$ solution. Report as potassium iodide.

Notes. Instead of adding bromine water, vapors of Br_2 can be introduced into the flask by drawing air through a little liquid bromine contained in a gas-washing bottle. Carry the vapors through glass tubing which ends in a small orifice just above the liquid in the flask.

Small quantities of bromide do not interfere, but if more than 20 times as much bromide as iodide is present, the results will be low. Ferric ions interfere by reacting with iodide, but the interference can be prevented by adding phosphoric acid.

As little as 1 mg of nitrite interferes, but interference can be prevented by the azido method of Reith.[1]

(c) Sodium Nitrite Method

In the presence of acid, the following reaction takes place completely:

$$2NO_2^- + 2I^- = 2NO + I_2 + 2H_2O$$
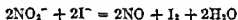
The excess nitrite and the nitric oxide must be removed before attempting to titrate the liberated iodine. This can be accomplished conveniently by means of urea:

$$2NO_2^- + CO(NH_2)_2 + 2H^+ = 2N_2 + CO_2 + 2H_2O$$
$$6NO + 2CO(NH_2)_2 = 5N_2 + 2CO_2 + 2H_2O$$
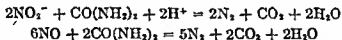
Since the reaction between nitrite and iodide takes place more rapidly than the reaction between nitrous acid and urea, it is possible to add the urea at the start. Chloride does not interfere, but if more bromide than is equivalent to the weight of iodide is present, the results will be high.

Procedure. Weigh out to the nearest tenth of a milligram about 0.4 g of sample into a 250-ml glass-stoppered bottle. Add about 1 g of urea, 8 ml of approximately 0.5 M sodium nitrite solution, and 5 ml of 4 N sulfuric acid. Stopper the bottle and allow it to stand with frequent shaking for about 10 minutes. Add 2 g of potassium iodide to dissolve the iodine as KI_3 and titrate with 0.1 N $Na_2S_2O_3$. Stopper the bottle frequently and shake to dissolve any iodine vapor. Starch indicator solution can be added toward the last, but this is unnecessary

[1] J. F. Reith, *Rec. trav. chim.*, 48, 386 (1929).

if about 10 ml of CCl_4 is added at the start. The shaking then helps to remove the iodine from the organic solvent.

15. Iodimetric Analysis of Chromite

Principle. The chromium of chromite, $FeCr_2O_4$, is oxidized to Na_2CrO_4 by fusion with sodium peroxide. The melt is leached with water, and the insoluble residue is dissolved in hydrochloric acid, added in slight excess. Ammonium fluoride is then added to convert Fe^{+++} into FeF_6^{---}; the former ions are reduced by hydriodic acid but the latter are unaffected. Then to the acid solution an excess of potassium iodide is added and the liberated iodine is titrated with sodium thiosulfate solution in the presence of starch as indicator.

$$2FeCr_2O_4 + 7Na_2O_2 \rightarrow 2NaFeO_2 + 4Na_2CrO_4 + 2Na_2O \text{ (fusion)}$$
$$\left. \begin{array}{l} NaFeO_2 + 2H_2O \rightarrow Na^+ + Fe(OH)_3 + OH^- \\ 2Na_2O_2 + 2H_2O \rightarrow 4Na^+ + 4OH^- + O_2 \end{array} \right\} \text{ (water added)}$$
$$\left. \begin{array}{l} 2CrO_4^{--} + 2H^+ \rightarrow Cr_2O_7^{--} + H_2O \\ Fe(OH)_3 + 3H^+ \rightarrow Fe^{+++} + 3H_2O \end{array} \right\} \text{ (acid added)}$$
$$Fe^{+++} + 6F^- \rightarrow FeF_6^{---} \text{ (fluoride added)}$$
$$Cr_2O_7^{--} + 6I^- + 14H^+ \rightarrow 2Cr^{+++} + 3I_2 + 7H_2O \text{ (iodide added)}$$
$$I_2 + 2S_2O_3^{--} \rightarrow 2I^- + S_4O_6^{--} \text{ (titration)}$$
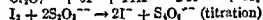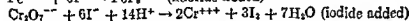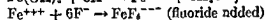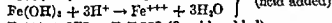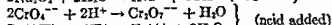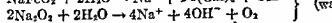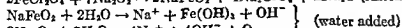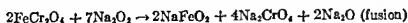
From these equations, it is evident that the milliequivalent weight of chromium is the atomic weight divided by 3000 as in the analysis with potassium dichromate (p. 582).

For the fusion, an iron crucible of about 25-ml capacity is commonly used. A nickel crucible is attacked less by the peroxide fusion, and the presence of nickel has been found advantageous for the decomposition of the excess peroxide, but it is usually necessary to filter the solution after making it acid when a nickel crucible is used, and the nickel crucible costs considerably more. A porcelain crucible has also been recommended, but this again is more expensive than the iron. The fusion can also be carried out in a test tube.

Procedure. Weigh out 0.3–0.4 g of chromite and fuse with sodium peroxide exactly as described on p. 582. Continue as directed there down to the point where the solution is made acid. Then, instead of sulfuric acid, add hydrochloric acid until all the hydrated ferric oxide has dissolved. Use 1 ml of concentrated hydrochloric acid in excess for each 100 ml of solution. Add 2 g of ammonium fluoride, more if necessary, until a small drop of the solution will give no test for Fe^{+++} with potassium ferrocyanide solution on the spot plate. Add 3 g of potassium iodide, wait 3 minutes, and then titrate with sodium thiosulfate solution. Add starch solution toward the last.

16. Analysis of Soluble Chromates

A concentrated, acid solution of potassium iodide is treated with a weighed amount of the chromate, diluted with water, and the liberated iodine titrated. (Cf. standardization of sodium thiosulfate against potassium dichromate, p. 588.)

17. Determination of Lead Peroxide

$$1 \text{ l of } 0.1 \ N \ Na_2S_2O_3 = 11.96 \text{ g } PbO_2$$

Method of Diehl, modified by Topf[1]

The analysis depends upon the fact that lead peroxide is reduced by means of potassium iodide in acetic acid solution when considerable alkali acetate is present:

$$PbO_2 + 4HI = PbI_2 + 2H_2O + I_2$$
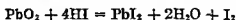
After diluting with water the iodine is titrated with $0.1 \ N \ Na_2S_2O_3$ solution.

Procedure. Dissolve about 0.5 g of the substance with 1.2 g of potassium iodide and 10 g of sodium acetate in 5 ml of 5 per cent acetic acid. Dilute the solution with water to a volume of 25 ml and titrate with sodium thiosulfate.

Remark. Moist lead peroxide reacts almost instantly on undergoing the above treatment; thoroughly dried material, on the other hand, dissolves after a few minutes provided that it is finely ground. If the dry peroxide is in the form of coarse grains, however, it may be several hours before the reaction is finished, or the decomposition may be incomplete.

Furthermore, too much potassium iodide should not be used, as otherwise lead iodide will separate out. In that event add 3-5 g more of sodium acetate and a few milliliters of water. Shake until the lead iodide has dissolved completely, and then dilute to a volume of 25 ml. The solution must remain perfectly clear and there should not be a trace of lead iodide precipitate.

This excellent method may also be used for the analysis of minium (red lead) or pyrolusite.

18. Determination of Ozone in Ozonized Oxygen

$$1 \text{ l of } 0.1 \ N \ Na_2S_2O_3 = \frac{O_3}{20} = 2.4 \text{ g } O_3$$

(a) Schönbein's Method

The most accurate method for estimating ozone consists in allowing the ozonized oxygen to act upon potassium iodide solution whereby free iodine is formed:

$$2KI + O_3 + H_2O = 2KOH + I_2 + O_2$$
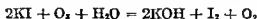
and the iodine may be titrated, after acidifying the solution with dilute sulfuric acid, by means of $0.1 \ N$ sodium thiosulfate.

It makes a difference, however, whether the ozone reacts with a *neutral* or with an *acid* solution of potassium iodide. In the latter case far too much iodine is liberated, although in the former case exactly the right amount is set free. Sir B. C. Brodie[2] called attention to this fact in his classic researches on ozone. Brodie

[1] Diehl, *Dinglers Polytech. J.*, 246, 196, and Topf, *Z. anal. Chem.*, 26, 296 (1887).

[2] *Phil. Trans.*, 162, 435-484 (1872).

confirmed the results obtained in his titrations by weighing the amount of ozone used in the experiments   This work of Brodie's appears to have been forgotten,[1] for many other chemists have since that time attempted to work out an iodimetric method for estimating ozone, some using acid and some neutral solutions to absorb the gas, although for a long time it occurred to no one else that the results could be checked by weighing out a definite amount of ozone for test experiments. In 1901, however, this was done in a very simple way by R. Ladenburg and R Quasig,[2] who were without knowledge of Brodie's work.   Their method consisted in weighing a glass bulb of known capacity which was provided with glass stopcocks, filling it with oxygen, and then weighing.   The oxygen was then replaced by ozone, so that *the gain in weight multiplied by 3 represented the amount of ozone present.*

In order, now, to titrate the ozone, Ladenburg and Quasig expelled the gas from the bulb by distilled water, and conducted it slowly through a *neutral* solution of potassium iodide which was subsequently treated with an equivalent amount of sulfuric acid and the liberated iodine titrated with N sodium thiosulfate.

The results of Ladenburg and Quasig have been carefully tested in the author's laboratory[3] and the method improved somewhat by absorbing the ozonized oxygen in the glass bulb itself rather than expelling the gas from the bulb and passing it into an iodide solution.

The estimation of ozone by weighing is a much too roundabout process to permit a practical application, particularly on account of the fact that the measurement and weighing of the gas must take place in a room at constant temperature, a condition which often cannot be readily fulfilled.   Consequently the volumetric titration of the gas is far more practical.

Procedure. Procure a glass bulb of about 390–400 ml capacity, of the form shown in Fig. 89, and determine its volume accurately by weighing it empty and then fill with water, applying the correction for temperature as described on pp. 435 *et seq.* Connect the bulb with a gas delivery tube, making use of Babo flanged joints (Fig. 89, *c* and *d*) pressing them together by means of a steel clamp, lined with cork (Fig. 90). Connect the delivery tube with the supply of ozone and oxygen, and replace the water in the bulb with the gas. During the filling of the bulb, but little of the ozone is absorbed by the water. When the tube is filled, close the lower stopcock first and the upper one a few seconds later. Then disconnect the bulb with the gas delivery tube, invert, open the upper stopcock quickly for an instant to establish atmospheric pressure in the bulb, and connect by means of rubber tubing with the gas reservoir N which is filled with $2 N$ potassium iodide solution (Fig. 91). Allow the air imprisoned in the rubber tubing to escape through the three-way stopcock *b*, and after properly setting the cock, introduce 20–30 ml of the iodide solution into the bulb. Finally close the stopcock *b* and disconnect the rubber tubing. Shake the

[1] Luther and Inglis, *Z. physik. Chem.*, **48**, 208 (1903).
[2] *Ber.*, **34**, 1184 (1901).
[3] Treadwell and Anneler, *Z. anorg Chem.*, **48**, 86 (1905).

contents of the bulb vigorously and allow to stand for half an hour; at the end of this time the absorption of the ozone will be complete.

Place an Erlenmeyer flask under the stopcock b'; open this and immediately afterwards the upper stopcock also. Wash out the bulb first by introducing some potassium iodide solution through a and finally
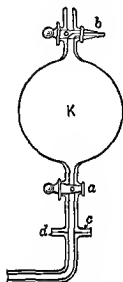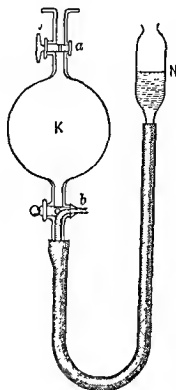
FIG. 89.　　　FIG. 90.　　　FIG. 91.

with pure water. Make the contents of the flask acid with dilute sulfuric acid and titrate the liberated iodine with 0.1 N sodium thiosulfate.

The computation is as follows: Assume the bulb to hold V ml; the weight of ozone found by titration $= p$ g; the temperature $= t°$; the barometer reading $= B$ ml, and the tension of water vapor $= w$.

The volume of the bulb at 0° and 760 mm pressure is

$$V_0 = \frac{V(B - w)\,273}{760\,(273 + t)}\ \text{ml}$$

When filled with oxygen this would weigh:

$$\frac{0.032 V_0}{22.41}\ \text{g}$$

Therefore the weight of oxygen and ozone in the bulb is

$$\frac{0.032 V_0}{22.41} + \frac{p}{3}$$

and the percentage of ozone in the mixture is

$$\frac{100p}{\dfrac{0.032 V_0}{22.41} + \dfrac{p}{3}} = \frac{6723p}{0.096 V_0 + 22.41p} = \text{per cent ozone}$$

(b) Method of Soret-Thenard[1]

Ozone is absorbed quantitatively by means of sodium arsenite solution in accordance with the following equation:

$$Na_2HAsO_3 + O_3 = Na_2HAsO_4 + O_2$$
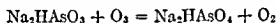
although A. Ladenburg[2] finds that the absorption takes place much more slowly than by means of potassium iodide. When, therefore, the ozone is passed through the arsenite solution, there is danger of getting too low results. If the absorption takes place in a glass bulb, however, the results are good.

Ozone is also absorbed by alkali bisulfite[3] solutions and may be estimated in this way, by titrating the excess of bisulfite with iodine. Ladenburg,[4] however, has shown that the method is not so accurate as the potassium iodide one, so that it will not be considered further here.

19. Determination of Hydrogen Peroxide. Kingzett's Method[5]

$$1 \text{ l of } 0.1 \text{ N } Na_2S_2O_3 \text{ solution} = \frac{H_2O_2}{20} = 1.7008 \text{ g } H_2O_2$$

The hydrogen peroxide solution is diluted until its H_2O_2 content corresponds to about 0.6 per cent by weight, and of this solution 10 ml is used in the analysis.

Procedure. Place about 2 g of potassium iodide in an Erlenmeyer flask and dissolve in 200 ml of water. Add 30 ml of 18 N sulfuric acid, and then, with constant stirring, introduce 10 ml of the hydrogen peroxide solution from a pipet. After allowing to stand for 5 minutes, titrate the iodine liberated with 0.1 N thiosulfate solution.

$$H_2O_2 + 2KI + H_2SO_4 = K_2SO_4 + 2H_2O + I_2$$
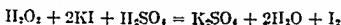
[1] Compt. rend., 38, 445 (1851); 75, 171 (1872).
[2] Ber., 36, 115 (1903).
[3] Neutral alkali sulfite is not suitable here, because it is not oxidized quickly by pure oxygen alone.
[4] Loc. cit.
[5] J. Chem. Soc., 1880, 792.

of the filtrate amounts to about 75 ml, receiving it in a 150-ml beaker. Take a strip of aluminum about 2.5 cm wide and 14 cm long, bend it into a triangle, and place it in the beaker resting on its edge. Cover the beaker and boil gently for 7–10 minutes, which will be sufficient to precipitate all the copper, provided that the solution does not much exceed 75 ml. Avoid boiling to a very small volume. The aluminum should now appear clean, the copper being detached or loosely adhering. Remove from the heat, and wash down the cover and sides of the beaker with hydrogen sulfide water. This will prevent oxidation and will also serve to precipitate the last traces of copper. If the hydrogen sulfide shows that more than a very little copper remained in solution, it is best to dilute the solution to 75 ml again and to boil a little longer. This will coagulate the sulfide. Finally, decant through a filter and then, without delay, transfer the precipitate to the filter with the aid of a stream of hydrogen sulfide water from a wash bottle. Let the strip of aluminum remain in the beaker, but wash it as clean as possible with the hydrogen sulfide water. Wash the filter and precipitate at least 6 times with this hydrogen sulfide water, but take care not to let the filter remain empty for any length of time. Moist copper sulfide oxidizes very rapidly when in contact with the air with the formation of a little copper sulfate, which will dissolve and pass through the filter only to precipitate again when it comes in contact with the filtrate containing hydrogen sulfide.

Now place the original clean flask under the funnel, perforate the filter, and rinse the precipitate into the flask with hot water, using as little as possible. Lift the fold of the filter and rinse down any precipitate found beneath the fold. Using a small pipet, allow 5 ml of strong nitric acid to run over the aluminum in the beaker and pour it from the beaker through the filter into the flask, but do not wash the beaker or filter at this stage. Remove the flask and replace it with the beaker. Heat the contents of the flask to dissolve the copper and expel the red fumes, then again place the flask under the funnel. Now pour over the filter 5 ml or more of bromine water, using enough to impart a strong color to the solution in the flask. Next wash the beaker and aluminum, pouring the washings through the filter. Finally wash the filter 6 times with hot water. Boil till the solution is reduced to about 25 ml, cool somewhat, and add a slight excess of strong ammonia (about 7 ml). Boil off the excess of ammonia, add an excess of acetic acid, and boil a minute longer. Cool to room temperature, add 3 g of potassium iodide, and titrate with sodium thiosulfate solution, adding starch toward the last.

(b) Method of Park

Dissolve the sample exactly as described in the above method of de Haën-Low and continue exactly as described there but receive the filtrate obtained after heating to fumes of H_2SO_4, diluting and filtering off the unsoluble residue, in a 250-ml Erlenmeyer flask. Concentrate to about 30 ml, cool, and add ammonium hydroxide until a slight permanent precipitate (usually $Fe(OH)_3$) is formed or the solution begins to turn a permanent blue. Heat if necessary to remove excess ammonia. Add 2 g of ammonium bifluoride, weighed to the nearest centigram, and 1 g of potassium acid phthalate, also weighed to the nearest centigram. When the solution is clear, add approximately 3 g of potassium iodide and titrate at once with thiosulfate solution, adding starch toward the last.

With the above conditions the pH of the solution is about 4 and antimony or arsenic is not reduced by the iodide. Ferric iron is not reduced because it is present for the most part as FeF_6^{---} anions.

2. Analysis of Arsenic Acid

The titration can take place in exactly the same way as in the standardization of 0.1 N iodine solution (see p. 590).

23. Determination of Antimony Trioxide Compounds

$$1 \text{ liter of } 0.1 \text{ N iodine solution} = \frac{Sb_2O_3}{40} = 7.289 \text{ g } Sb_2O_3 = 6.089 \text{ g } Sb$$

The titration is carried out exactly as with arsenious acid (cf. p. 590) except that tartaric acid, or Rochelle salt, must be added to the solution in order to prevent the precipitation of antimonous acid, or antimony oxychloride, as a result of hydrolysis.

Examples:

(a) Determination of Antimony in Tartar Emetic

$$1 \text{ liter of } 0.1 \text{ N iodine solution} = \frac{K(SbO)C_4H_4O_6 + \frac{1}{2}H_2O}{20} = 16.70 \text{ g}$$

If an aqueous solution of tartar emetic is treated with iodine in the presence of starch, the first few drops of reagent will impart a permanent blue color to the solution. If, however, a little sodium bicarbonate is added to the solution, the trivalent antimony is oxidized quantitatively to the quinquevalent condition.

$$K(SbO)C_4H_4O_6 + 6NaHCO_3 + I_2 =$$
$$Na_2SbO_4 + 2NaI + KNaC_4H_4O_6 + 3H_2O + 6CO_2$$
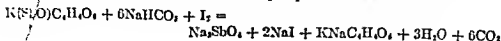
Dissolve 8.350 g of tartar emetic in water, dilute the solution to exactly 500 ml, and mix well. Of this solution, transfer 20 ml with a pipet into 100 ml of water containing 0.5 g of sodium bicarbonate. Titrate with 0.1 N iodine solution, using starch as an indicator.

(b) Determination of Antimony in Stibnite

1 ml of normal iodine solution = 0.06088 g Sb

Principle. Stibnite, Sb_2S_3, dissolves in 12 N normal hydrochloric acid with evolution of hydrogen sulfide.

$$Sb_2S_3 + 8HCl \rightarrow 2HSbCl_4 + 3H_2S \uparrow$$
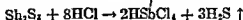
After the hydrogen sulfide has been removed, tartaric acid is added to form the antimonyl tartrate ion, which is so stable that it prevents the hydrolysis of the antimony salt upon dilution:

$$SbCl_4^- + H_2C_4H_4O_6 + H_2O \rightarrow H(SbO)C_4H_4O_6 + 3H^+ + 4Cl^-$$
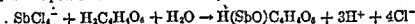
The final titration takes place as follows:

$$H(SbO)C_4H_4O_6 + I_2 + 2HCO_3^- \rightarrow H(SbO_2)C_4H_4O_6 + 2I^- + H_2O + 2CO_2 \uparrow$$
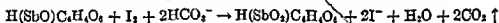
Weigh out 0.2–0.3 g of stibnite into a 150-ml beaker, cover with a watch glass, and add 10 ml of concentrated hydrochloric acid. Allow the acid to act in the cold for 10 minutes, add 0.3 g of solid potassium chloride, and heat gently on the water bath for 15 minutes to complete the attack and expel hydrogen sulfide. Take care not to allow the liquid to evaporate sufficiently to expose any part of the bottom of the beaker. There is usually a silicious residue, insoluble in hydrochloric acid.

Remove the beaker from the water bath, cool to room temperature, and add a solution of 3 g of tartaric acid which has been dissolved by heating in a test tube with 5 ml of water and cooled under running water. Mix well by rotating the contents of the beaker. Slowly add water, while stirring, to a volume of about 100 ml.

Pour this solution slowly, while stirring, into a 600-ml beaker containing 10 g of sodium carbonate dissolved in 200 ml of cold water. This serves to neutralize the acid and provide sufficient sodium bicarbonate to keep the solution neutral during the iodine titration. Wash down the sides of the beaker, add starch paste, and titrate with iodine to the appearance of a permanent blue.

If a fugitive end point is obtained, SbOCl has been precipitated or not enough sodium bicarbonate is present.

Remarks. Antimony chloride is volatile with steam from its concentrated hydrochloric acid solutions, but the heating on the water bath can be carried out, without

fear of losing antimony, if the acid is not allowed to evaporate too much and KCl is present in form less volatile KSbCl$_4$. This heating serves to remove all the hydrogen sulfide which would otherwise precipitate the antimony as trisulfide upon diluting the solution. If insufficient tartaric acid is present, antimony oxychloride, SbOCl, precipitates; and if the solution is titrated in this condition it is impossible to obtain a permanent end point.

24. Determination of Antimony Pentoxide Compounds (A. Weller)[1]

By heating a quinquevalent antimony compound with concentrated hydrochloric acid and potassium iodide in the Bunsen apparatus (Fig. 88, p. 598), the antimonic acid is reduced with separation of iodine:

$$H_3SbO_4 + 5H^+ + 2I^- \rightarrow Sb^{+++} + 4H_2O + I_2$$
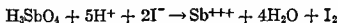
The iodine is distilled over into potassium iodide solution and titrated with 0.1 N Na$_2$S$_2$O$_3$ solution. The results are a little low.

25. Determination of Hydrogen Sulfide

$$1 \text{ l of } 0.1 \text{ } N \text{ Na}_2\text{S}_2\text{O}_3 \text{ solution} = \frac{\text{H}_2\text{S}}{20} = 1.704 \text{ g H}_2\text{S}$$

If an acid solution of hydrogen sulfide is treated with iodine, the sulfide is oxidized with separation of sulfur: $H_2S + I_2 = 2HI + S$. The solution must not react basic as then some sulfide will be oxidized to sulfate and some iodine will react with OH$^-$ to form iodide and iodate ions.

For the determination of the amount of the gas present in hydrogen sulfide water, transfer a measured amount by means of a pipet to a known volume of 0.1 N iodine solution and titrate the excess of the latter with thiosulfate solution.[2]

If the amount of hydrogen sulfide present is not very large, correct results are obtained without difficulty. With considerable hydrogen sulfide, on the other hand, the deposited sulfur is likely to enclose some of the iodine solution, as shown by its brown color; this iodine escapes the titration with thiosulfate. In such a case, remove the film of sulfur floating on the surface of the liquid with a glass rod after the completion of the thiosulfate titration, transfer it to a glass-stoppered cylinder, and shake with 1–2 ml of carbon disulfide. This dissolves the iodine with a violet color, and the color can be discharged with sodium thiosulfate

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[1] *Ann. Chem. Pharm.*, 213, 364.

[2] Correct results cannot be obtained by titrating directly with iodine; cf. O. Brunck, *Z. anal. Chem.*, 45, 541 (1906).

solution.[1] In this way the total amount of the iodine that remains can be titrated.

Remark. This method can be used to advantage for determining the sulfur ent in soluble sulfides.

Determination of Hydrogen Sulfide in Mineral Waters

Place a measured amount of 0.01 N iodine solution and 2 g of potassium iodide in a tall liter cylinder, add 1 l of the water to be analyzed, and, after thoroughly shaking, titrate the excess of the iodine with 0.01 N thiosulfate. The iodine solution used is standardized by measuring off 10 ml of the solution, adding 2 g of potassium iodide, diluting to 1 l with boiled water, and titrating with 0.01 N thiosulfate solution.

Remark. The hydrogen sulfide in a water is not always present as free gas but may be present as hydrosulfide, i.e., as HS^- anions. The mineral water will also contain free carbonic acid and HCO_3^- anions. According to the mass-action law:

$$(1) \quad \frac{[H^+] \times [HS^-]}{[H_2S]} = 0.91 \times 10^{-7} \quad \text{and} \quad (2) \quad \frac{[H^+] \times [HCO_3^-]}{[H_2CO_3]} = 3.04 \times 10^{-7}$$

Since the two equilibria are both satisfied in the solution, the hydrogen-ion concentrated is the same in each expression. $[H^+] = \dfrac{0.91 \times 10^{-7} \times [H_2S]}{[HS^-]}$, and inserting this value in equation (2) we have

$$(3) \quad \frac{[HS^-]}{[H_2S]} = 0.3 \frac{[HCO_3^-]}{[H_2CO_3]}$$

In all these equations the symbols in brackets represent moles per liter of the substance.

With the aid of equation (3) it is possible to compute the quantity of free hydrogen sulfide present in a sample of mineral provided that a complete analysis of the water has been made.

Let C = the total millimoles per liter of non-ionized H_2CO_3 and HCO_3^-, let S = the total millimoles per liter of HS^- and non-ionized H_2S, and let d = the difference between the total milliequivalents of cations per liter and of the anions with the exception of HCO_3^- and HS^-. Then $d = [HS^-] + [HCO_3^-]$, $S = [HS^- + H_2S]$ and $C = d + [H_2CO_3] - [HS^-]$.

From this it follows:

$$[HS^-] = S - [H_2S]$$
$$[HCO_3^-] = d - [HS^-] = d - S + [H_2S]$$
$$[H_2CO_3] = C - d + [HS^-] = C - d + S - [H_2S]$$

---

[1] The separation of the sulfur into a coherent film can be prevented by sufficiently diluting the solution with boiled water. O. Brunck (*Z. anal. Chem.*, 45, 541) therefore, recommends using 0.01 N iodine instead of 0.1 N solution, and this is certainly advisable with small quantities of hydrogen sulfide as, for example, in a mineral water. On the other hand, when a relatively large volume of hydrogen sulfide is liberated from a sulfide by means of acid it is advisable to use 0.1 N iodine, as otherwise the volume of solution will be too large unless a very small weight of substance is used in the analysis.

Substituting these values in equation (3) we get:

$$\frac{S - [H_2S]}{[H_2S]} = 0.3 \frac{d - S + [H_2S]}{C - d + S - [H_2S]}$$

and by solving the equation

$$(4) \quad [H_2S] = \frac{(1.7S - C - 0.7d) \pm \sqrt{(1.7S + C - 0.7d)^2 - 2.8S(S + C - d)}}{1.4}$$

= millimoles of free H_2S per liter.

This value multiplied by 0 03109 gives the weight of free H_2S in grams.

26. Analysis of Alkali Sulfides

1 l of 0.1 N iodine solution $= \dfrac{R_2S}{20}$ or $\dfrac{S}{20} = 1.603$ g S

Allow a measured volume of the alkali sulfide solution to run slowly, with constant stirring, into 300–400 ml of water, an excess of iodine, and hydrochloric acid.[1] Titrate the excess of iodine with sodium thiosulfate solution.

Remark. The solution of sulfide cannot be titrated directly in the iodine.

27. Analysis of Mixtures of Alkali Sulfide, Alkali Hydrosulfide, and Hydrogen Sulfide

1 l of 0.1 N iodine solution $= \begin{cases} 1.704 \text{ g } H_2S \\ 2.803 \text{ g } NaHS \\ 3 903 \text{ g } Na_2S \end{cases}$

Principle. If a solution of alkali sulfide and alkali hydrosulfide is treated with an acid solution of iodine, the following reactions take place:

(a) $Na_2S + 2HCl = 2NaCl + H_2S$
(b) $NaSH + HCl = NaCl + H_2S$
(c) $H_2S + I_2 = 2HI + S$
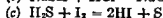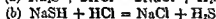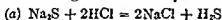
Hydrogen sulfide is a very weak acid, without effect upon phenolphthalein indicator. After oxidation, the hydrogen sulfide is replaced by the strong mineral acidhydriodic acid.

It is evident from the above equations that in the case of the sulfide, the quantity of hydriodic acid formed by the ___ ___ quantity of hydrochloric acid ___ hydrosulfide, however, which is the acid salt of hydrogen sulfide, the quantity of hydriodic acid formed is equivalent to twice the quantity of hydrochloric acid required to decompose the hydrosulfide.

By determining the quantity of acid or base present at the start, the acidity at the end of the analysis, and the quantity of iodine used in ___ ___ sulfur, one can distinguish that any strong acid pre

---

[1] To determine how much acid is necessary, titrate a trial sample with methyl orange as indicator with 6 N hydrochloric acid.

The reasoning applies, of course, to cases where other strong acids or other bases are present. The solution may contain:

(1) Sodium hydroxide, NaOH, and sodium sulfide, Na_2S.
(2) Sodium sulfide alone.
(3) Sodium sulfide, Na_2S, and sodium hydrosulfide, NaHS.
(4) Sodium hydrosulfide alone.
(5) Sodium hydrosulfide, NaHS, and hydrogen sulfide, H_2S.
(6) Hydrogen sulfide alone.
(7) Hydrogen sulfide, H_2S, and hydrochloric acid, HCl.

Any other possibility is excluded because sodium hydroxide and sodium hydrosulfide react to form sodium sulfide; sodium sulfide and hydrogen sulfide react to form sodium hydrosulfide; sodium hydrosulfide and hydrochloric acid react to form hydrogen sulfide. We may regard these last three reactions as taking place practically completely because there is a great difference in the ionization constants of HCl, H_2S and HS^-.

Now let us consider what will happen in the analysis of the seven mixtures just mentioned. In the analysis let us assume that a milliequivalents of iodine solution together with b milliequivalents of hydrochloric acid are added at the start. The excess iodine is titrated with c milliequivalents of sodium thiosulfate, and after that d milliequivalents of sodium hydroxide are added to make the solution neutral to phenolphthalein. From these four values, a, b, c, and d, we can easily compute the quantity of NaOH, Na_2S, NaHS, H_2S, and HCl originally present, but, as just explained, the only possible combinations will be two neighboring compounds, NaOH and Na_2S, Na_2S and NaHS, NaHS and H_2S, H_2S and HCl.

(1) In this case, the hydrochloric acid added at the beginning of the analysis will be neutralized by both NaOH and Na_2S. The quantity of iodine required will be equivalent to the sulfide present, and, since the weak hydrogen sulfide becomes strong hydriodic acid, just as much hydriodic acid will be formed as was required of hydrochloric acid to liberate hydrogen sulfide from the sodium sulfide.

$$a - c = \text{milliequivalents of sulfide present}$$

$$b - d = \text{milliequivalents of NaOH}$$

The molecular weight of Na_2S divided by 2000 is the milliequivalent weight of Na_2S.

(2) In the second case, when sodium sulfide alone is present, $b = d$ and $a - c =$ milliequivalents of sulfide as in case (1).

(3) When sodium sulfide and sodium hydrosulfide are both present, the relations are a little more complicated. As in the previous cases, $a - c =$ the milliequivalents of sulfide present, and the milliequivalents of sodium sulfide and of sodium hydrosulfide from the standpoint of iodimetry are the molecular weights divided by 2000 in each case. The value d in this case is greater than b; $d - b =$ the milliequivalents of NaHS present and $a - c > 2(d - b)$ because the milliequivalent weight of sodium hydrosulfide from the acidimetric standpoint is one-thousandth of the molecular weight. Therefore, if we subtract from $a - c$ (the total milliequivalents of iodine required for Na_2S and NaHS) twice the value of $d - b$, the difference will be the milliequivalents of Na_2S present.

(4) Here $a - c = 2(d - b)$. The NaHS content can be computed from either $a - c$ or from $d - b$, but we must remember to divide the molecular weight of NaHS by 2000 if we wish to find the milliequivalent from the iodimetric standpoint and by 1000 if we wish to find the milliequivalent from the acidimetric standpoint.

(5) When NaHS and H_2S are present, $a - c < 2(d - b)$. Here, as in every other case, the milliequivalent of each sulfide is the molecular weight divided by 2000 from the iodimetric standpoint. With respect to the HI formed by the action of iodine, the milliequivalent weight of NaHS is the molecular weight divided by 1000, but with hydrogen sulfide it is the molecular weight divided by 2000 exactly as in the iodine titration. If we call n_1 the number of millimoles of NaHS and n_2 the millimoles of H_2S, then

$$2n_1 + 2n_2 = a - c$$

$$n_1 + 2n_2 = d - b$$

(6) When hydrogen sulfide alone is present

$$a - c = d - b$$

(7) When hydrogen sulfide and hydrochloric acid are present, $a - c < d - b$. From the value of $a - c$ the quantity of H_2S can be computed, and by subtracting $a - c$ from $d - b$ the milliequivalents of HCl present are found.

In any case, therefore, all we have to do is to compare the milliequivalents of iodine with the milliequivalents of acid or base required to neutralize the solution after the iodine titration. Calling the former value T_1 ($a - c$ in the above notation) and the latter value T_2 ($d - b$ in the above notation), the above seven cases can be summarized as follows:

(1) In determining T_2, we find that $b > d$. The solution contains NaOH and Na_2S.

(2) $T_2 = 0$. Na_2S alone is present.

(3) $T_1 > 2T_2$. Na_2S and NaHS are present.

(4) $T_1 = 2T_2$. NaHS alone is present.

(5) $T_1 < 2T_2$. NaHS and H_2S are present.

(6) $T_1 = T_2$. H_2S alone is present.

(7) $T_1 < T_2$. H_2S and HCl are present.

One naturally inquires at this point whether such a study is of great importance. No such claim can be made. There is really no need for asking a student to carry out such an analysis in the laboratory in an elementary course of instruction. C~ ~¹ ~' ~ ~ ~ ~ ~ ~ ~
relations, for s ~ ~ ~ ~ ~ ~ ~ ~
stands what is
great difficulty in following the above reasoning. Confusion arises from the fact that the milliequivalent weight varies in accordance with the nature of the chemical reaction involved. The mathematical computations involve nothing more difficult than elementary algebra.

Procedure. Dilute a known volume of 0.1 N iodine together with a known volume of 0.1 N hydrochloric acid¹ in a beaker to a volume of about 400 ml, and slowly add the solution containing the dissolved sulfide from a buret with constant stirring, until the mixture becomes pale yellow. Add starch indicator and titrate the excess of iodine with tenth-

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¹ Enough acid to decompose all sulfide must be present. An excess does no harm.

normal thiosulfate solution. Finally, titrate the acid in the solution with 0.1 N sodium hydroxide solution, using phenolphthalein as indicator. Calculate the results as outlined above.

28. Determination of Sulfur in Steel by the Evolution Method

Transfer 5 g of steel borings to a 250-ml flask which is fitted with a rubber stopper carrying a thistle tube that extends nearly to the bottom

of the flask and a Kjeldahl distilling bulb which ends just below the surface of the stopper (Fig. 92). This bulb acts as a splash trap. Connect the outside end of the bulb with glass tubing that reaches nearly to the bottom of a 200-ml Erlenmeyer flask. Connect the latter with a second Erlenmeyer flask. In each of the Erlenmeyer flasks place 50 ml of water and 10 ml of either of the following ammoniacal absorbents.
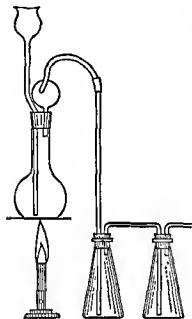
Ammoniacal Zinc Sulfate. Dissolve 20 g of $ZnSO_4\cdot 7H_2O$ in 100 ml of water, and to the solution add an equal volume of concentrated ammonium hydroxide. Filter after standing over night.

Ammoniacal Cadmium Chloride. Dissolve 12 g of $CdCl_2\cdot 2H_2O$ in 150 ml of water and to the solution add 60 ml of concentrated ammonium hydroxide. Filter if not clear.

Fig. 92.

Pour 80 ml of 6 N HCl through the thistle tube of the evolution flask and heat so that there is a rapid and steady evolution of gas. When all the steel has dissolved, boil for 30 seconds, but never long enough to cause much HCl to pass over into the other flasks. The first flask should contain all the sulfur of the steel as white ZnS or as yellow CdS. The second flask is used merely to make sure that no H$_2$S escapes unabsorbed. Filter off the sulfide precipitate, and wash out the flask twice with dilute NH$_4$OH (approximately 0.5 N). Transfer the filter and precipitate to a beaker, and cover with 300 ml of water. Rinse out the delivery tubing, where there is any sulfide, with 50 ml of N HCl, and add this solution to the liquid in the beaker containing the precipitate. At once add a measured volume of standard iodine solution (10 ml of 0.05 N solution is usually sufficient and should be added from a pipet), and after a few minutes titrate the excess iodine with sodium thiosulfate solution to a starch end point (see p. 588).

Unless the relative strengths of the two solutions have been checked recently, add 10 ml of the iodine solution from a pipet to 300 ml of water to which 5 ml of concentrated HCl has been added and titrate with thiosulfate to a starch end point.

In this analysis, the milliequivalent weight of sulfur is 0.016 g. Standardize the solutions by any method described on pp. 586–591.

Most cast irons do not give up all their sulfur by this method of analysis. The values are nearer the truth if the sample is annealed as follows: Wrap 5 g of sample in two 11-cm filter papers so that all the metal is under at least 3 thicknesses of paper. Place in a 25-ml porcelain crucible, cover with a well-fitting lid, and heat 30–40 minutes at about 750°. Cool slowly, and transfer the charred paper and steel to the evolution flask. With high-silicon irons, heat the acid rapidly to boiling and then allow to simmer.

If selenium is present, all or a part of it is evolved as H_2Se. If a mixture of H_2S and H_2Se is passed through 60 ml of the following special reagent, the H_2Se is absorbed but the H_2S is not. After this the H_2S is absorbed as usual.

Special Reagent for H_2Se. Mix 10 g of ZnO with water and dissolve in as little 6 N HCl as is convenient. Add 50 g of KCl and dilute to 1 l. Add dilute KOH until a portion of the solution gives a yellow color when tested with thymol blue indicator, then add carefully dilute HCl until the color obtained in the test is a full red. This reagent absorbs H_2Se but not H_2S.

Remark. Instead of 0.05 N iodine solution a solution of 1.12 g KIO_3 and 12 g KI in a liter of water is often used. This mixture furnishes iodine when added to dilute acid;

$$5KI + KIO_3 + 6HCl = 3I_2 + 6KCl + 3H_2O$$

It is 0.0314 N with respect to iodine and 1 ml = 0.000503 g S if the KIO_3 is pure and the weighing is exact to three significant figures.

29. Determination of Thiosulfate in the Presence of Sulfide and Hydrosulfide

Treat a measured volume of the solution in a 200-ml measuring flask with an excess of freshly precipitated cadmium carbonate. Shake well and dilute the liquid to the mark. Filter through a dry filter, reject the first 20 ml of filtrate, and titrate 100 ml with iodine solution. By shaking with cadmium carbonate, the sulfide and hydrosulfide are precipitated as yellow CdS and the thiosulfate remains in solution.

30. Determination of Sulfurous Acid

$$1 \text{ l of } 0.1 \text{ N iodine solution} = \frac{SO_2}{20} = 3.203 \text{ g } SO_2$$

The determination is based upon the following reaction:

$$SO_2 + 2H_2O + I_2 = 4H^+ + 2I^- + SO_4^{--}$$
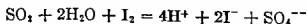
the sulfurous acid being oxidized to sulfuric acid. If starch is added to a solution of sulfurous acid, and a titrated iodine solution is run into it from a buret, the blue color will not be obtained until all the sulfurous acid has been acted upon. Bunsen, however, in 1854 showed that this sensitive reaction, which was first used by Dupasquier, will take place quantitatively according to the above equation only when the solution does not contain more than 0.04 per cent by weight of SO_2. With greater concentrations uniform results are not obtained.

Correct results are always obtained if the sulfurous acid is added slowly, with constant stirring, to the iodine solution until the latter is decolorized.

In the analysis of sulfites, add the sulfite solution from a buret to the solution of iodine and hydrochloric acid.

31. Determination of Formaldehyde (Formalin). Method of G. Romijn[1]

$$1 \text{ l of } 0.1 \text{ N iodine solution} = \frac{HCHO}{2} = 15.01 \text{ g formaldehyde}$$

Principle. Formaldehyde is oxidized quantitatively to formic acid by remaining in contact with iodine for a short time in alkaline solution:

$$HCHO + H_2O + I_2 = 2HI + HCOOH$$
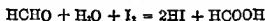
Procedure. The aqueous solution of formaldehyde, known commercially as "formalin," contains about 40 per cent of formaldehyde. For analysis, dilute 10 ml of the formaldehyde solution to 400 ml, and of this 1 per cent solution, take 5 ml (= 0.125 ml of the original solution) for analysis. Add 40 ml of 0.1 N iodine solution, and immediately afterwards strong sodium hydroxide solution, drop by drop, until the color of the solution is a light yellow; allow to stand for 10 minutes. Then make the solution acid with hydrochloric acid, and titrate the excess iodine with 0.1 N sodium thiosulfate.

32. Determination of Ferricyanic Acid[2]

$$1 \text{ l of } 0.1 \text{ N iodine solution} = \frac{K_3Fe(CN)_6}{10} = 32.92 \text{ g } K_3Fe(CN)_6$$

Principle. If a neutral solution of potassium ferricyanide is treated with an excess of potassium iodide, the ferricyanide ion is reduced to ferrocyanide ion with separation of free iodine:

$$2K_3Fe(CN)_6 + 2KI \rightleftharpoons 2K_4Fe(CN)_6 + I_2$$
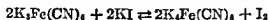
[1] *Z. anal. Chem.*, **36**, 19 (1897).

[2] Lenssen, *Ann. Chem.*, **91**, 240. Mohr., *ibid.*, **105**, 60.

Lenssen titrated the liberated iodine with sodium thiosulfate, but the results are not concordant, because the reaction is a reversible one. The reaction is quantitative, however, as Mohr first showed, if the ferrocyanide is removed from the solution as fast as it is formed. This is accomplished, according to Mohr, by adding an excess of zinc sulfate, free from iron, to the solution. According to the experiments of E. Müller and O. Diefenthäler,[1] the titration should take place in a solution which is as nearly neutral as possible, but not in one made alkaline by the addition of sodium bicarbonate; some $NaIO$ is formed.

Müller and Diefenthäler's Procedure. Weigh out 0.7 g of the ferricyanide into a glass-stoppered flask, dissolve in about 50 ml of water, and treat with 3 g of potassium iodide and 1.5 g of zinc sulfate free from iron. If an acid solution of ferricyanide is to be analyzed, carefully neutralize with caustic soda until barely alkaline and then made acid with a drop of sulfuric acid. Alkaline solutions must always be neutralized with acid.

33. Determination of Ferri- and Ferrocyanide in the Presence of One Another

In one sample determine ferricyanide iodimetrically as just described and in another sample determine ferrocyanide by permanganate titration (p. 564).

D. POTASSIUM IODATE, POTASSIUM BROMATE, AND CALCIUM HYPOCHLORITE METHODS

POTASSIUM IODATE

Potassium iodate, KIO_3, and potassium biiodate, $KH(IO_3)_2$ are good oxidizing agents but the iodate ion has a lower oxidation potential than the other oxidizing agents, with the exception of iodine, which have been discussed up to this point, and iodates are expensive. The chief uses of these iodates in titration methods is as standards in alkalimetry, acidimetry, and iodimetry. The iodates are also useful for preparing solutions containing known quantities of iodine, for the reaction

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$$

takes place completely in the presence of sufficient iodide and acid. The iodates can be prepared in a very pure state and are easier to weigh out and dissolve than iodine. In strong hydrochloric acid, iodate is reduced quantitatively to iodine monochloride, rather than to iodine.

$$IO_3^- + 2I^- + 6H^+ + 3Cl^- = 3ICl + 3H_2O$$
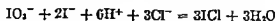
The iodine monochloride is not very stable and is readily reduced to free iodine. It is often used as a catalyzer in oxidation titrations; when the reducing agent is in

[1] Z. anorg. Chem., 1910, 418.

excess free iodine is liberated, and when enough of the oxidizer has been added to react with all the reducing agent, the iodine disappears (cf. p. 636 and below). If the concentration of hydrochloric acid is at least 3 N, potassium iodate can be used for the titration of alkali iodide, free iodine, arsenite, hydrazine, sulfurous acid, etc., in accordance with the following equations:[1]

$$2I^- + IO_3^- + 6H^+ + 3Cl^- \rightarrow 3ICl + 3H_2O$$
$$2I_2 + IO_3^- + 6H^+ + 5Cl^- \rightarrow 5ICl + 3H_2O$$
$$2As^{+++} + IO_3^- + Cl^- + 5H_2O \rightarrow 2H_3AsO_4 + ICl + 4H^+$$
$$N_2H_4 + IO_3^- + 2H^+ + Cl^- \rightarrow N_2 + ICl + 3H_2O$$
$$2H_2SO_3 + IO_3^- + Cl^- \rightarrow 2SO_4^{--} + ICl + H_2O + 2H^+$$
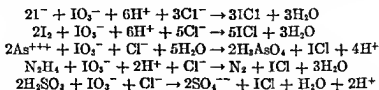
Instead of high concentrations of hydrochloric acid, the above reactions can be carried out in 0.5 N sulfuric acid when potassium cyanide is added.[2] In this case iodine cyanide, instead of iodine monochloride, is formed:

$$IO_3 + 2I^- + 3H^+ = 3ICN + 3H_2O$$
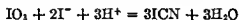
Determination of Copper with Potassium Iodate[3]

L. W. Andrew[4] has shown that quite a number of substances capable of reducing iodate, such as free iodine, iodides, arsenites, and antimonites, can be titrated with potassium iodate very exactly, by taking advantage of the fact that, when the reducing agent is present in excess, free iodine is formed which is oxidized quantitatively by more iodate, provided that the proper amount of hydrochloric acid is present. Copper solutions are precipitated quantitatively by potassium thiocyanate and sulfurous acid as cuprous thiocyanate, CuSCN, and Parr[5] has estimated copper quantitatively by titrating this precipitate with permanganate. The oxidation is simpler and more accurate, however, when the titration is effected by potassium iodate or biiodate. The reaction goes through the stage in which iodine is set free, but the iodine is oxidized completely to iodine chloride upon the addition of more iodate:

(a) $10CuSCN + 14KIO_3 + 14HCl = 10CuSO_4 + 7I_2 + 10HCN + 14KCl + 2H_2O$

(b) $2I_2 + KIO_3 + 6HCl = KCl + 5ICl + 3H_2O$
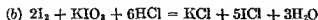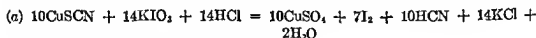
and the whole reaction is

(c) $4CuSCN + 7KIO_3 + 14HCl = 4CuSO_4 + 7ICl + 4HCN + 7KCl + 5H_2O$

The potassium iodate solution is very stable and can be preserved for years if protected from evaporation. The standard solution used can be prepared by weighing out a known amount of the pure salt and dissolving to a definite volume, or the solution can be standardized against pure copper, carrying out the process as in an analysis. A convenient concentration is $\frac{1}{24}$ mole KIO_3 per liter.

[1] See G. S Jamieson, *Volumetric Iodate Methods*, New York, 1926.

[2] R. Lang, *Z. anorg. allgem. Chem.*, **122**, 332 (1922); 142, 229, 279 (1925); **144**, 75 (1925).

[3] Jamieson, Levy, and Wells, *J. Am. Chem. Soc.*, **30**, 760 (1908).

[4] *Ibid.*, 25, 756 (1903).

[5] *Ibid.*, 22, 685 (1900).

Procedure. To 0.5 g of the ore in a 200-ml flask, add 6–10 ml of strong nitric acid, and boil gently, preferably over a free flame, keeping the flask in constant motion and inclined at an angle of about 45°, until the larger part of the acid has been removed. If this does not completely decompose the ore, add 5 ml of strong hydrochloric acid and continue the boiling until the volume of liquid is about 2 ml. Now add gradually and carefully, after cooling somewhat, 12 ml of 18 N sulfuric acid, and continue the boiling until sulfuric acid fumes are evolved copiously. Allow to cool, add 25 ml of cold water, heat to boiling, and keep hot until the soluble sulfates have dissolved. Filter into a beaker, and wash the flask and filter thoroughly with cold water. Nearly neutralize the filtrate with ammonia and add 10–15 ml of strong sulfur dioxide water. Heat just to boiling and add 5–10 ml of a 10 per cent solution of ammonium thiocyanate, according to the amount of copper present. Stir thoroughly, allow the precipitate to settle for 5 to 10 minutes, filter on paper, and wash with hot water until the excess ammonium thiocyanate is removed completely.

Place the filter with its contents in a glass-stoppered bottle of about 250-ml capacity, and by means of a piece of moist filter paper transfer into the bottle any precipitate adhering to the stirring rod and beaker. Add to the bottle about 5 ml of chloroform, 20 ml of water, and 30 ml of concentrated hydrochloric acid (the two last liquids may have been mixed previously). Now run in standard potassium iodate solution, inserting the stopper and shaking vigorously between additions. A violet color appears in the chloroform, at first increasing and then diminishing, until it disappears with great sharpness. The rapidity with which the iodate solution may be added can be judged from the color changes of the chloroform.

To make another titration it is not necessary to wash the bottle or throw away the chloroform. Pour off two-thirds or three-fourths of the liquid in order to remove most of the pulped paper, too much of which interferes with the settling of the chloroform globules after agitation, add enough properly diluted acid to make about 50 ml, and proceed as before. In this case, where iodine monochloride is present at the outset, the chloroform becomes strongly colored with iodine as soon as the cuprous thiocyanate is added, but this makes no difference in the results of the titration.

Determination of Lead and Arsenic in Commercial Lead Arsenate

Two methods for determining lead and three methods for determining arsenic in this important insecticide will be described, which are taken

from the *Proceedings of the Official Agricultural Chemists of the United States.*

If the sample is in the form of a paste dry the whole of it on the water bath to get the water content. Grind the residue to a fine powder and dry at 110–120° to constant weight. Use this for the following analyses.

(a) **Determination of Lead as Sulfate.** Dissolve 2 g of the dry powder in 80 ml of 2.5 N nitric acid. Heat on the water bath until all the lead arsenate is dissolved. Transfer to a 250-ml measuring flask and dilute to the mark at 20°. To 50 ml of the solution, add 3 ml of concentrated sulfuric acid and evaporate till dense fumes of sulfuric acid are evolved. This is best accomplished by heating in a 250-ml Erlenmeyer flask. Allow to cool; cautiously add 50 ml of water and 100 ml of 95 per cent alcohol. Allow to stand several hours, then filter and wash 10 times with a mixture of 3 parts concentrated sulfuric acid, 200 of alcohol, and 100 of water by volume. Ignite and weigh as lead sulfate (p. 58).

Remark. If the sample contains any alkaline earth, the lead sulfate will be very impure and should be purified as directed on p. 59.

(b) **Determination of Lead as Chromate.** Dissolve 0.6906 g of dry powder in 25 ml of 3 N nitric acid. Filter if necessary. Dilute to 400 ml, heat to boiling, and add ammonia water until a slight permanent precipitate is formed. Dissolve this precipitate with a little 1.5 N nitric acid and add 2 ml in excess. To the hot solution, add from a pipet 5 ml of 10 per cent potassium chromate solution. Allow the precipitate of lead chromate to settle, filter into a Gooch crucible, wash with hot water till free from alkali chromate, dry at 140–150°, and weigh as $PbCrO_4$. The weight of the precipitate in grams multiplied by 100 gives the percentage of PbO present.

(c) **Determination of Arsenic by Modified Gooch-Browning Method.** Take 100 ml of the nitric acid solution prepared as described in (a), add 6 ml of concentrated sulfuric acid, and evaporate to fumes. Cool, transfer to a 100-ml measuring flask with cold water and make up to the mark at 20°. Mix thoroughly by pouring back and forth into a dry beaker, allow the precipitate to settle in the stoppered flask, and then decant the clear solution through a dry filter. After rejecting the first runnings, take 50 ml of the filtrate; add 4 ml of concentrated sulfuric acid and 1 g of potassium iodide. Dilute to about 100 ml and boil until the volume is reduced to about 40 ml. In this way the arsenic acid is reduced to the trivalent condition and iodine is liberated. Do not carry the evaporation too far, or attempt to boil off the last traces of liberated iodine. Arsenic iodide is reddish and colors the concentrated

solution very much the same as a little iodine does. It is volatilized if the solution is evaporated too far.

Cool the solution under running water, dilute to about 300 ml, and carefully add sodium thiosulfate solution until all the free iodine is reduced to colorless iodide, adding starch paste toward the end. At this dilution, the color of arsenic iodide is not apparent. To the acid solution add 15 g of anhydrous sodium carbonate in small portions and titrate with 0.1 N iodine solution. One milliliter 0.1 N I_2 solution = 0.003749 g of As.

Remark. Inasmuch as iodine reacts with sodium hydroxide to form hypoiodite and iodide, it is generally recommended to finish the neutralization with sodium bicarbonate solution. This is unnecessary, however, because sodium bicarbonate is formed by the reaction between acid and the normal carbonate and as long as free carbon dioxide is present in the solution, there is no danger. The quantity of sodium carbonate added should be greater than 1 and less than 2 moles for each mole of sulfuric acid present, and 2-3 g of bicarbonate, formed from the normal carbonate, should remain unneutralized.

(d) Determination of Arsenic by the Distillation Method. Provide a 250-ml distilling flask with a long-stem, 50-ml dropping funnel and connect it to a 60-cm Liebig condenser. Connect the outlet of the condenser to a 500-ml Erlenmeyer flask by a short bent tube extending about 10 cm below the bottom of the three-hole stopper which closes the flask. Through the middle hole in this stopper insert a 50-cm piece of straight tubing so that it reaches to within about 1 cm from the bottom of the flask and acts as a safety tube. Through the third hole introduce a twice-bent glass tube starting from just below the stopper and leading nearly to the bottom of a second 500-ml Erlenmeyer flask with a two-hole stopper. Through the second hole insert a twice-bent tube leading to a 250-ml Erlenmeyer flask. Place 50 ml of water in the first flask, 100 ml in the second, and 50 ml in the third, and surround the first two flasks with cracked ice. The third flask acts merely as a trap, and no arsenic chloride should reach it.

Weigh 0.4-0.6 g of the dry powder and 5 g of cuprous chloride directly into the distilling flask, taking care not to let any powder get into the distilling arm. Add 100 ml of concentrated hydrochloric acid from the dropping funnel and start distilling. When the volume of liquid in the distilling flask has been reduced to 40 ml, add 50 ml more of acid and again distil to 40 ml. Finally add 25 ml more of concentrated hydrochloric acid and distil until only 20 ml is left in the distilling flask. This procedure ensures the complete volatilization of all the arsenic as trichloride from 0.6 g of commercial insecticides.

After the distillation is completed, rinse out the connecting tubes

and transfer the contents of the first two absorption flasks to a 500-ml measuring flask, and make up to the mark at 20°.

To 100 ml of the mixed solution add 15 g of sodium hydroxide dissolved in a little water, and finish the neutralization by adding sodium carbonate until the solution is alkaline to methyl orange. Then add 2 g of sodium bicarbonate and titrate with iodine (p. 590).

(e) Determination of Arsenic by the Potassium Iodate Method of G. S. Jamieson.[1]

In a solution containing trivalent arsenic in the presence of 11–20 per cent of hydrogen chloride, arsenic can be accurately titrated by means of potassium iodate solution (cf. p. 624):

$$2AsCl_3 + KIO_3 + 5H_2O \rightarrow 2H_3AsO_4 + KCl + ICl + 4HCl$$
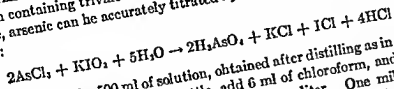
Transfer 100 ml of the 500 ml of solution, obtained after distilling as in the previous method, to a 250-ml glass-stoppered bottle, add 6 ml of chloroform, and titrate with standard KIO_3 solution containing 3.244 g KIO_3 per liter. One milliliter of this solution reacts with 3 mg of As_2O_3. If more than 25 ml of the iodate solution is needed, add 10–15 ml more of concentrated hydrochloric acid before finishing the titration, in order to maintain the proper acidity. The end point is explained on p. 625.

To determine arsenic present as *arsenite* in any insecticide: Weigh out 0.14–0.4 g of the powder, depending upon the arsenic content, into a 250-ml glass-stoppered bottle. Add 30 ml of concentrated hydrochloric acid, 20 ml of water, and 6 ml of chloroform. Titrate at once with the iodate solution. Titrate rapidly at first, while shaking the bottle so as to give a gyratory motion to the contents. When the iodine liberated during the first part of the titration has largely disappeared from the solution, insert the stopper, shake well, and from this point add the reagent slowly, shaking after each addition. Finally wait 5 minutes after the color is discharged from the chloroform to see if it returns.

POTASSIUM BROMATE METHODS

Potassium bromate, $KBrO_3$, is very much like potassium iodate in its reactions and has been used a great deal as a standard in iodimetry. Just as iodate and iodide are used for preparing definite quantities of iodine, so have bromate and bromide been used to prepare definite quantities of bromine. Liquid bromine is unpleasant to handle and the advantages of the bromide-bromate mixture are obvious. Free bromine can be detected by its color with the aid of carbon tetrachloride but a more sensitive indicator, in the absence of other oxidizers, is methyl orange or methyl red. These indicators have a red color in dilute acid solutions but the color is destroyed by free bromine. The color change of the indicator is not reversible as the indicator is decomposed by the oxidation. The oxidation of the indicator, especially in strongly acidic solutions and at higher temperatures, is quite rapid, and for that reason there is some danger of the indicator's losing its color where there is a local excess of oxidizer before the end point has been reached. Other dyestuffs can be used instead of methyl orange or methyl red.[2]

[1] J. Ind. Eng. Chem., 10, 290 (1918).
[2] G. F. Smith and H. H. Bliss, J. Am. Chem. Soc., 53, 2091 (1931).

Direct titration with potassium bromate solution has been used for oxidizing trivalent arsenic or antimony to the quinquevalent state and for oxidizing univalent thallous to trivalent thallic ions. Hydrazine is oxidized to free nitrogen as with iodate. Koppeschaar's method for titrating phenols will be described below, and similar oxidations have been applied to the bromination of many other organic compounds. One of the most important applications is the titration of magnesium after its precipitation with 8-hydroxyquinoline (oxine). A similar titration can serve for any other oxine precipitate (e g , Al, Fe, Zn, Ni, Cu, Mn).

A standard 0.1 N KBrO₃ solution can be easily obtained by dissolving 2 783 g of pure KBrO₃ in water, diluting to exactly 1000 ml in a volumetric flask, and mixing. Sometimes about 10 g of pure KBr is dissolved together with the bromate, but usually the bromide is added to the solution to be titrated. If there is any doubt about the purity of the potassium bromate, the solution can be standardized against arsenic trioxide.

Standardization of KBrO₃ against As₂O₃. Weigh out to the nearest 0.1 mg about 0 2 g of pure As₂O₃ (equivalent weight 49.45) into a 250-ml Erlenmeyer flask. Dissolve in Na₂CO₃ solution and neutralize with HCl as described on p 591. Dilute to about 50 ml; add 15 ml of concentrated HCl, 0.5 g KBr, and 1 or 2 drops of 0 1 per cent methyl orange indicator solution. Titrate slowly with the bromate while keeping the solution mixed by constant swirling. Toward the last add the bromate dropwise with a few seconds' interval between drops until the color changes sharply from red to colorless or pale yellow. Mix well and add another drop of indicator to make sure that the end point is reached.

Determination of Arsenic

$$1 \text{ l of } 0.1 \text{ } N \text{ KBrO}_3 = \frac{\text{KBrO}_3}{60} = 2.783 \text{ g KBrO}_3 = 4.948 \text{ g As}_2\text{O}_3$$

Principle. If a hydrochloric acid solution of arsenious acid is treated with potassium bromate, the arsenic is completely oxidized to arsenate. As soon as all the arsenic is oxidized, the next drop of potassium bromate solution causes separation of bromine.

$$3Na_2HAsO_3 + KBrO_3 + 6HCl = 6NaCl + KBr + 3H_3AsO_4$$
$$KBrO_3 + 5KBr + 6HCl = 6KCl + 3H_2O + 3Br_2$$
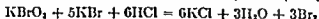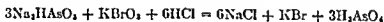
If the solution contains methyl orange it will show an acid reaction as long as arsenic is present, but free bromine destroys the indicator and the solution becomes colorless at the end point.

Determination of Antimony

Potassium bromate method can be used for oxidizing trivalent antimony to the quinquevalent state. The procedure is similar to that described for the determination of antimony in Babbitt metal (p. 104) except that KBrO₃ is used instead of KMnO₄. The presence of methyl orange, which is decolorized at the end point, is desirable. (Cf. "Standardization of KBrO₃ solution against As₂O₃.")

Determination of Alkali Sulfides with Potassium Bromate[1]

$$1 \, l \text{ of } 0.1 \, N \, KBrO_3 = \frac{H_2S}{80} = 0.4260 \text{ g } H_2S$$

$$H_2S + 4H_2O + 4Br_2 = 8HBr + H_2SO_4$$

Place the measured sample of solution in the liter bottle shown in Fig. 93, which is provided with a ground-glass stopper carrying a drop-

FIG. 93.

ping funnel. Add a considerable excess of 0.1 N potassium bromate solution and 3–4 g of potassium bromide. Evacuate the bottle with a water suction pump and close the stopcock. Pour hydrochloric acid in the funnel and allow it to flow into the bottle by carefully opening the stopcock. When the solution is distinctly acid, close the stopcock and shake the contents of the bottle. To effect a good oxidation, the solution should contain 25 per cent of concentrated hydrochloric acid by volume. At first the solution assumes a brown color, then the color fades but should remain distinctly yellow. A slight turbidity of sulfur disappears in 10–15 minutes, being oxidized to sulfuric acid.

When the solution is perfectly clear, wash out the funnel with a little water but avoid letting air enter. Add 2–3 g of potassium iodide dissolved in a little water and shake. Rinse out the funnel and titrate with sodium thiosulfate solution.

If T is the volume of 0.1 N bromate solution used and t the volume of 0.1 N thiosulfate, then $(T - t)$ 0.0004260 g H_2S is present.

This method is a little more complicated than direct titration with iodine, but as the oxidation of the sulfur is from sulfide to sulfate, 4 times as much oxidizing agent is required. The method is suitable for the titration of hydrogen sulfide in the presence of thiocyanate.

Determination of Alkali Sulfide in the Presence of Alkali Thiocyanate

The reactions involved in the method are illustrated by the following equations:

(a) $\begin{cases} H_2S + 4H_2O + 4Br_2 = 8HBr + H_2SO_4 \\ HCNS + 4H_2O + 3Br_2 = H_2SO_4 + HCN + 6HBr \end{cases}$

(b) $H_2S + I_2 = 2HI + S$
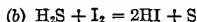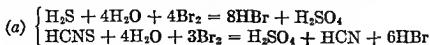
In one sample determine the total sulfur content by the method just

[1] Treadwell and Mayr, Z. anorg. Chem., 92, 127 (1915).

described, and in another sample determine the sulfide iodimetrically (p. 617). If the total 0.1 N potassium bromate solution used was T ml, and if t ml of 0.1 N thiosulfate was used for titrating the excess and t_1 ml of 0.1 N iodine solution was used for the direct titration of sulfide in the same weight of substance, a g, then

$$\frac{[(T - t) - 4t_1]0.0968}{a} = \text{per cent CNS}$$

and

$$\frac{t_1 \times 0.1603}{a} = \text{per cent S (as sulfide)}$$

Determination of Tin with Potassium Bromate[1]

$$1 \text{ l of } 0.1 \text{ N KBrO}_2 = \frac{\text{Sn}}{20} = 5.935 \text{ g Sn}$$

Place 20 ml of faintly acid stannous or stannic solution (about 6 g of tin per liter) in a 200-ml flask, add 0.15 g of aluminum wire in short pieces, and allow the reaction to proceed in the cold until all the tin is precipitated. Add 30 ml of concentrated hydrochloric acid and 20 ml of water, and stopper the flask with a Bunsen valve (p. 540). Heat gently till all the tin has dissolved. Cool and titrate with 0.1 N potassium bromate solution until a permanent yellow color is obtained.

$$3Sn^{++} + BrO_3^- + 6H^+ = 3H_2O + Br^- + 3Sn^{++++}$$
$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O$$
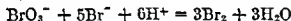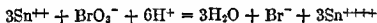
Remark. Boller obtained low results when testing pure tin. He has improved the method by adding a slight excess of bromate, then some potassium iodide, and finally titrating with sodium thiosulfate. The results are about 1 per cent too low if air is present in the solution. Boller proceeds as follows:

Place 100 ml of 7 N hydrochloric acid in the 500-ml flask shown in Fig. 94 and boil 5 minutes to expel air, with stopcock A open and B closed. Remove the flame and quickly introduce the weighed sample of metallic tin and a little piece of calcite to furnish carbon dioxide gas. Replace the top piece and, with B open, boil gently until all the tin is dissolved. Then close B and cool the contents of the flask with cold water. This produces a partial vacuum in the flask.
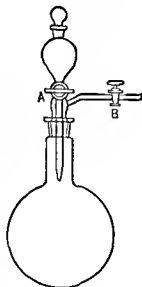
Fig. 94.

[1] Method of H. Zschokke. Cf. Fiechter and Mueller, *Chem. Ztg.*, **37**, 309 (1913); St. Györy, *Z. anal. Chem.*, **32**, 415 (1893).

While the tin is dissolving prepare a mixture of 50 ml of 0.1 N $KBrO_3$ solution, 1 g of potassium bromide, and a little water. Boil 5 minutes to expel air. Pour this solution into the funnel of the above-mentioned flask and allow it to flow into the stannous solution by carefully opening the stopcock A. The stannous chloride is oxidized instantly to stannic salt. Rinse out the contents of the funnel with boiled water, add 10 ml of 5 per cent potassium iodide solution, and titrate with 0.1 N thiosulfate.

The tin determination as originally given by Zschokke gives good results if the bromate solution is standardized against tin in the same way that the analysis is made.

Determination of Thiocyanate. Method of Treadwell-Mayr

$$1 \text{ l of } 0.1 \ N \ KBrO_3 \text{ solution} = \frac{HCNS}{60} = 0.9847 \text{ g HCNS}$$

In acid and neutral solution thiocyanate does not react with iodine but in alkaline solution the following reaction takes place:

$$CNS^- + 8OH^- + 4I_2 = SO_4^{--} + 7I^- + CNI + 4H_2O$$

The reaction takes place very slowly. Oxidation is effected much more rapidly with a bromate-bromide solution in the presence of hydrochloric acid:

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$
$$HCNS + 3Br_2 + 4H_2O \rightarrow HCN + SO_4^{--} + 6Br^-$$
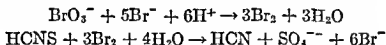
Procedure. Treat a measured volume of thiocyanate solution with a measured volume of 0.1 N potassium bromate solution and 2-3 g of potassium bromide in the liter bottle shown in Fig. 94, p. 631. Evacuate with suction and close the stopcock. Introduce 30-40 ml of 6 N hydrochloric acid for each 100 ml of solution without letting in any air. Shake well. After standing 10 minutes, rinse out the funnel with water and add 2-3 g of potassium iodide dissolved in a little water. Shake and then titrate the liberated iodine with 0.1 N thiosulfate.

If T is the volume of 0.1 N bromate solution and t the volume of 0.1 N thiosulfate, then

$$(T - t) \frac{HCNS \times 100}{60,000 \times a} = \frac{(T - t) \ 0.09847}{a} \text{ per cent HCNS}$$

Determination of Phenol. Method of W. Koppeschaar[1]

$$1 \text{ l of } 0.1 \ N \ Na_2S_2O_3 = \frac{C_6H_5OH}{60} = 1.568 \text{ g } C_6H_5OH$$

Principle. If an aqueous solution of phenol is treated with an excess of bromine, the phenol is converted quantitatively into tribromophenol:

$$C_6H_5OH + 3Br_2 = 3HBr + C_6H_2Br_3(OH)$$
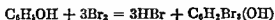
The tribromophenol is a pale yellow crystalline substance which is quite insoluble in water (43.7 l of water dissolves 1 g of tribromophenol). If, after the reaction has taken place, potassium iodide is added to the solution, iodine is liberated corresponding to the excess of bromine, and by titrating this iodine with sodium thiosulfate solution, it is easy to find how much bromine reacted with the phenol.

Procedure. Weigh out 5 g of phenol in a weighing beaker, dissolve in a little water, rinse the solution into a liter flask, and shake well. Of this solution, pipet off 100 ml, transfer to another liter flask, dilute with water to the mark, mix and transfer 100 ml of this solution to a stoppered bottle of about 250-ml capacity, treat with 50 ml of 0.1 N $KBrO_3$ solution and 0.5 g of KBr, shake, make acid with 5 ml of concentrated hydrochloric acid, shake again, and allow to stand 15 minutes. Then add 2 g of potassium iodide and titrate the liberated iodine, corresponding to the excess of bromine, with 0.1 N thiosulfate solution, using starch as indicator. Then if t ml of the last solution is used and the weight of phenol was a g:

$$\frac{(50 - t) \times 0.1568}{a} = \text{per cent phenol}$$

Remark. This method is suitable for the analysis of pure preparations of phenol (carbolic acid) but not for crude phenol, creosote oil, etc.

Determination of Magnesium

8-Hydroxyquinoline reacts with 2 molecules of bromine to form a dibromo substitution product

$$HO \cdot C_9H_4N + 2Br_2 = HO \ C_9H_4Br_2 + 2HBr$$

The graphic formula of the dibrominated product is
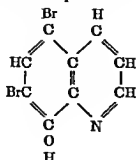
[1] Z. anal. Chem., 15, 233 (1876).

The precipitates produced with this reagent have the general formula $Me(C_9H_6ON)_n$ where n represents the valence of the cation Me. 8-Hydroxyquinoline (trivial name, *oxine*) can serve for the precipitation of copper, bismuth, cadmium, aluminum, and zinc in buffered acetic acid solutions and for magnesium in ammoniacal solution. Silver, mercury, lead, antimony, vanadium, uranium, iron, titanium, zirconium, tantalum, columbium, manganese, nickel, and cobalt as well as some other ions also give precipitates with oxine, and the reagent would be used a great deal more, for the precipitates are easy to handle, if it were more specific in its action. It has been used a great deal for precipitating aluminum, after Group II metals have been removed and a sodium hydroxide separation has been made, and for the determination of magnesium after all other ions except the alkalies have been removed. The oxine precipitate can be weighed (see p. 260) or it can be dissolved and brominated by treating with a measured volume of standard $KBrO_3$, an excess of KBr, and hydrochloric acid. After the bromination, the excess Br_2 (1 mole $KBrO_3 = 6Br$) can be determined iodimetrically by adding excess KI and titrating the liberated iodine with thiosulfate, or by adding a measured volume of sodium arsenite solution and titrating the excess with $KBrO_3$ solution.

Procedure. Prepare a slightly acid solution containing not more than 0 06 g Mg in 100 ml of solution and sufficient NH_4Cl (about 0.5 g) to prevent precipitation of $Mg(OH)_2$. Large quantities of ammonium salt interfere with the oxine precipitation. Heat to about 65°, and add 1 ml of oxine reagent for each 5 mg of Mg probably present and, in every case, 7 ml in excess. (To prepare the reagent, dissolve 25 g of the solid oxine in 50 ml of glacial acetic acid, pour the solution into 950 ml of water which has been heated to 60°, cool, and filter.) *Slowly* add 5 N ammonia solution to a distinctly ammoniacal reaction. If an excess of the reagent is present, the color of the solution will now be yellow. Let the precipitate settle, filter through paper, and wash the precipitate with cold, 0.35 N ammonia water. Dissolve the washed precipitate in hot 2 N HCl, and catch the solution, as it runs through the filter, in a 250-ml glass-stoppered bottle. Wash with the same acid until the washings are colorless. Dilute with the same acid to 50 ml; add 1 g of KBr and 2 to 4 drops of methyl red indicator solution. Titrate slowly, while keeping the solution in motion, until the color changes from red to yellow. Stopper the flask, allow to stand 2 minutes, add 1 g of KI, and titrate the liberated iodine with standard sodium thiosulfate solution.

Calcium Hypochlorite Method

Koltkoff and Stenger[1] have proposed the use of calcium hypochlorite solution as a standard oxidizing agent. The aqueous solution can be kept in dark glass bottles for some time without much change in titer.

Preparation of Approximately 0.1 N Solution. Add about 10 g of a good brand of commercial " chloride of lime " to 250 ml of distilled water, mix well, and filter. Dilute the filtrate to about 1 l. The formation of a turbidity of $CaCO_3$ on standing does no harm.

Standardization against Arsenic Trioxide. As indicator use a 0.2 per cent solution of Bordeaux (British Color Index No. 83). Pipet off 25 ml of standard 0.1 N sodium arsenite solution; add 1 g of KBr and 0.5 g of $NaHCO_3$. Titrate with the hypochlorite solution fairly rapidly until within a few milliliters of the expected end

[1] *Ind. Eng. Chem., Anal. Ed.*, 7, 79 (1935).

point. Add 1 drop of the indicator solution and titrate very slowly, while rotating the flask, until the color of the indicator fades. Add another drop of indicator, and if this does not fade also, add more hypochlorite until the color changes quickly from pink to colorless or light yellow. As indicator correction, subtract 0.03 ml of 0.1 N bypochlorite solution for the oxidation of each drop of indicator used.

DETERMINATION OF AMMONIA IN AMMONIUM SULFATE

The reaction

$$2NH_3 + 3BrO^- = N_2 + 3Br^- + 3H_2O$$
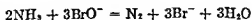
takes place rather slowly. It is best to add an excess of hypochlorite, then an excess of arsenite solution, and finish by titrating with hypochlorite as above.

Procedure. Dissolve about 1 g of ammonium sulfate (weighed to four significant figures) in water and dilute to exactly 250 ml in a volumetric flask. Mix well and pipet off 25 ml of the solution To this add 1 g of KBr and 0 5 g of NaHCO₃. Titrate with 0 1 N hypochlorite until a permanent light yellow color is obtained which indicates an excess of hypobromite. After waiting 5 minutes, add from a pipet exactly 10 00 ml of 0 01 N sodium arsenite solution; add 1 drop of Bordeaux indicator, and titrate with hypochlorite as in its standardization.

E. CERIC SULFATE METHODS

Cerium forms colorless cerous salts in which it has a valence of 3 and yellow or orange ceric salts in which it has a valence of 4. Cerous salts can be oxidized to ceric salts in acid solutions (a) by heating with lead dioxide and 5 N nitric acid, (b) by heating with ammonium persulfate, (c) by electrolysis, and (d) by sodium bismuthate.

$$2Ce^{+++} + PbO_2 + 4H^+ = 2Ce^{++++} + Pb^{++} + 2H_2O$$
$$2Ce^{+++} + S_2O_8^{--} = 2Ce^{++++} + 2SO_4^{--}$$
$$Ce^{+++} = Ce^{++++} + e$$
$$2Ce^{+++} + NaBiO_3 + 6H^+ = 2Ce^{++++} + Na^+ + Bi^{+++} + 3H_2O$$
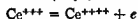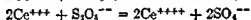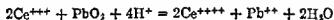
As a result of the oxidation, the colorless cerous solution becomes yellow or orange. If a solution of a cerous salt is treated with an excess of alkali hydroxide and chlorine gas is led through the solution, the white cerous hydroxide, Ce(OH)₃, which forms when the solution is made basic, is changed to light yellow ceric hydroxide, Ce(OH)₄. The precipitate of ceric hydroxide dissolves in nitric acid yielding a red solution, but when acted upon by hydrochloric acid, colorless cerous chloride is formed and chlorine is evolved as a result of the oxidation of some of the hydrogen chloride.

The normal potential corresponding to the reaction Ce⁺⁺⁺ = Ce⁺⁺⁺⁺ + e is +1.45 volts. If we compare this with the reaction Mn⁺⁺ + 4H₂O = MnO₄⁻ + 8H⁺ + 5e which has a normal potential of +1.52 volts and with the reaction 2Cr⁺⁺⁺ + 7H₂O = Cr₂O₇⁻⁻ + 6e which has a normal potential of +1.3 volts, we see that ceric sulfate is a stronger oxidizing agent than potassium dichromate and is nearly as strong as potassium permanganate. Ceric sulfate solutions are less sensitive to hydrochloric acid than are solutions of potassium permanganate, and there is but one possible reduction product. The oxidation potential varies with the character of the anion present. The above value 1.45 holds in sulfate solutions. It is 1.28 in chloride solutions, 1.61 in the presence of nitrate, and 1.70 for perchlorate.

A possible explanation is that the ceric ion is not present as such but in the form of a complex ion.

Were it not for the fact that ceric salts are much more expensive than equivalent quantities of permanganate, doubtless the use of these salts as oxidation agents would be far more prevalent. On the other hand, the cost of the reagent is by no means prohibitive, and it is already being used widely. Like permanganate and unlike potassium dichromate, the ceric salt is not suitable for use as a primary standard or, in other words, a standard solution cannot be obtained by weighing out an exact quantity of ceric sulfate.[1] The reagent should be prepared by dissolving approximately the proper quantity of ceric salt, and the solution should then be standardized by titration against sodium oxalate or a solution containing ferrous salt.

Ceric solutions, like those of potassium permanganate, can serve as their own indicators for the titration of colorless solutions, but the color change is not so marked and it requires a little more of the ceric solution to impart a perceptible tint to the fully titrated solution. The color change is more noticeable in hot solutions than in the cold. In the titration of ferrous salts with ceric sulfate it is best to add phosphoric acid to form the colorless ferric acid phosphate complex and to use ferrous orthophenanthroline as indicator. Diphenylamine sulfonic acid, diphenylbenzidine, and some similar organic compounds can also be used as indicators. These indicators form oxidation products which have colors easily distinguishable from the colors of the unoxidized compounds, and the oxidation-reduction potential is such that the organic compound is not oxidized until after practically all the substance being titrated has entered into the reaction; in other words, the color change takes place when the desired oxidation of the substance being analyzed has been completed.

In some reactions which take place readily with permanganate, a catalyst must be used with ceric solution. Thus the titration of oxalate is best accomplished with iodine monochloride, ICl, as catalyst, and the oxidation of arsenite can be catalyzed with OsO_4.

To prepare the iodine monochloride solution, dissolve 0.1395 g KIO_3 and 0.0890 g KI in 125 ml of water and at once add 125 ml of concentrated HCl. Cool to room temperature, add 5 ml of $CHCl_3$, and titrate carefully either with 0.1 N KIO_3 or KI until the chloroform layer shows only a very faint iodine after vigorous shaking in a glass-stoppered bottle. For 100 ml of solution to be titrated with $Ce(SO_4)_2$, add 2.5 ml of this solution and 1 drop of ferrous phenanthroline indicator solution. Diphenylamine sulfonate indicator can also be used.

Preparation of 0.1 N Ceric Sulfate Solution[2]

Ceric sulfate solutions can be prepared by digesting the oxide, CeO_2, with strong sulfuric acid at 125° or higher, cooling, and diluting. The solution after being diluted should be 1–2 N in sulfuric acid. Ceric oxide of suitable purity can be purchased as such, or it may be made by igniting cerous oxalate, which is one of the cheapest cerium salts, to 600–625° for about 10 hours.

[1] The compound $(NH_4)_2Ce...$ ... as a suitable standard in oxidimetry. Smi ... ...n. Soc., 50, 1322, 1334, 1372 (1918). Willard

[2] Willard and Yo ... .y. Chem., Anal. Ed., 8, 449 (1936).
and Furman, Elementary Quantitative Analysis.

It is far more convenient to use pure ceric ammonium sulfate, $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$, which can be purchased from dealers in chemicals and has the high molecular weight of 632.5. Weigh out approximately 65 g of the salt, add 500 ml of 2 N sulfuric acid, and stir till all the solid has dissolved. Dilute to about 1 l, mix well, and keep in a glass-stoppered bottle.

Standardization. Sodium oxalate, arsenic trioxide, or iron wire can be used for standardization. The reactions with oxalate and trivalent arsenic are slow, and the presence of a catalyst is desirable. For this purpose a little iodine monochloride is recommended for the oxalate titration and some osmium tetroxide, OsO_4, for the arsenite (3 drops of a solution obtained by dissolving 0.25 g OsO_4 in 100 ml of 0.1 N H_2SO_4).

(a) *Against Arsenic Trioxide.* Weigh out 0.15–0.22 g of pure As_2O_3 into a 250-ml Erlenmeyer flask, add 15 ml of 2 N NaOH, and heat gently to hasten the dissolving. When all the white powder has dissolved, cool to room temperature; add 25 ml of 6 N H_2SO_4, 3 drops of 0.01 M OsO_4 solution (see above), and 1 or 2 drops of ferrous phenanthroline indicator (1.5 g of o-phenanthroline monohydrate in 100 ml of freshly prepared 0.025 M ferrous sulfate solution). Titrate with approximately 0.1 N ceric ammonium sulfate solution until the reddish orange color of the indicator changes to colorless or very pale blue.

(b) *Against Pure Iron.* Weigh out accurately duplicate portions of about 0.25 g of iron wire (specially prepared for standardization) into 100-ml beakers; add to each 5 ml of water and 10 ml of concentrated hydrochloric acid. Heat gently until all the metal has dissolved. Unless particular precautions are taken to avoid oxidation (see p. 539) the solution will show a slight yellow color, due to the formation of a little ferric chloride as a result of atmospheric oxidation; hydrochloric acid alone can only oxidize iron to the ferrous state. To convert all the iron to the ferrous condition, carefully add stannous chloride solution (see p. 545) until the hot solution no longer shows any yellow color, but avoid adding an excess of the reagent. Cool by placing the beaker in running water, transfer to a 400-ml beaker, dilute to 150 ml, and add 10 ml of mercuric chloride solution (cf. p. 545). A white, silky precipitate of mercurous chloride should be formed. If the precipitate is dark in color or is bulky, it is best to throw the solution away and start again. To the ferrous solution add 10 ml of phosphoric acid, d 1.37, and 0.3 ml of 0.01 M diphenylamine sodium sulfonate. (To prepare this indicator solution, dissolve 0.32 g of the barium salt in 100 ml of water, add 0.5 g of solid sodium sulfate, stir well, and allow the barium sulfate precipitate to settle. Decant off the clear solution.) One or two drops of ferrous o-phenanthroline indicator solution can be used instead of the diphenyl-

amine sulfonate. Titrate with the ceric sulfate solution until the solution assumes a distinct purple tint. The reaction between the indicator and the ceric sulfate is rapid but not instantaneous; the reagent should he added slowly toward the last.

$$Fe^{++} + Ce^{++++} \rightarrow Fe^{+++} + Ce^{+++}$$
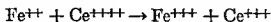
Determination of Iron in an Iron Ore

Dissolve 0.25–0.30 g of the powdered ore by heating gently with 20 ml of 6 N hydrochloric acid exactly as described on p. 581. After the reduction with stannous chloride and treatment with mercuric chloride, add 10 ml of phosphoric acid, d 1.37, and 0.3 ml of 0.01 M diphenylamine sodium sulfonate indicator solution. Titrate with ceric sulfate solution as just described for the standardization of the solution against pure iron.

Ceric sulfate can be used for many other oxidations. It oxidizes hydrogen peroxide, nitrous acid, hydrazine, hydroxylamine, hydrazoic acid, tartaric acid, oxalic acid, anthracene, sodium thiosulfate, sulfurous acid, and hypophosphorous acid as well as many other substances. Some of these reactions can be utilized for various titrations. Thus the oxidation of the oxalate ion can he used not alone for standardizing the ceric solution but also for determining cations like calcium, strontium, and lead which form insoluble oxalates. All the filtered precipitates yield oxalic acid, when digested with dilute acid, and the oxalic acid can he titrated with ceric sulfate.

Oxidation-Reduction Indicators

In the sections on potassium dichromate and ceric sulfate methods, the use of oxidation-reduction indicators (or *redox* indicators, as they are sometimes called) was advocated. Their action is in many respects comparable to that of acid-base indicators The oxidation-reduction indicators are organic compounds which change color when oxidized or reduced. This change in color takes place at definite oxidation potentials. The indicator reaction can be expressed by the reversible equation

$$I_{Ox} + ne \rightleftharpoons I_{Red}$$

where I_{Ox} represents the oxidized form and I_{Red} is the reduced form. The action of the indicator does not depend upon the specific nature of the oxidant or reductant but upon the relative oxidation potentials of the indicator and of the system titrated. Thus, for titrations of a ferrous salt with ceric sulfate, the indicator used should be chosen so that the indicator will not change color until all the ferrous salt has been oxidized, and the oxidation potential of the indicator reaction must lie between that of the ceric sulfate and that of the ferrous solutions. The oxidation-reduction indicators which are most used in common titrations are diphenylamine, dipbenyl-

benzidine, diphenylamine sulfonic acid. and phenanthroline-ferrous ion. Quite a number of other substances have been proposed and are now being studied.

Diphenylamine and diphenylbenzidine have been used widely. Both these compounds are sparingly soluble in water, and the indicator solutions are prepared by dissolving 1 g in 100 ml of concentrated sulfuric acid. A few drops of either solution suffices for a titration in a volume of 200–300 ml. Upon oxidation, diphenylamine, $C_6H_5 \cdot NH \, C_6H_5$, is changed to diphenylbenzidine, $(C_6H_5 \cdot NH \cdot C_6H_4)_2$. This reaction is not reversible, and both substances are colorless. Diphenylbenzidine is oxidized to a violet oxidation product called diphenylbenzidine violet,

$$C_6H_5 \cdot N : C_6H_4 : C_6H_4 : N \cdot C_6H_5$$

The normal oxidation potential of this reaction is +0.76 volt. These indicators can be used in titrations with permanganate, ceric sulfate, dichromate, and vanadato against ferrous sulfate, but the diphenylbenzidine violet is not stable toward oxidizing agents and is slowly but irreversibly oxidized further. The slight solubilities in water and the fact that they cannot be used in the presence of tungstate are handicaps. On the other hand, diphenylamine sulfonate is much more soluble in water and can be used in the presence of tungstate.

Diphenylamine sulfonic acid (cf. p. 578) gives a green color with ferrous salts which is probably caused by a combination of unoxidized diphenylamine sulfonic acid with some of the violet oxidation product. The violet color does not appear until all ferrous salt is oxidized. The oxidation of the indicator requires an appreciable quantity of 0.01 N oxidant, but the indicator correction is small in the case of 0.1 N solutions. The color change in titrating ferrous salts is sharp, but the reddish oxidation product is slowly decomposed on standing and the tint does not increase upon addition of excess oxidant. The color change is explained as in the case of diphenylbenzidine (see above).

Phenanthroline-Ferrous Ion. The organic base o-phenanthroline, $C_{12}H_8N_2$, dissolves easily in solutions of ferrous salts forming a red complex cation $Fe(C_{12}H_8N_2)_3^{++}$ of an intensely red color; strong oxidizing agents convert this ion to pale blue $Fe(C_{12}H_8N_2)_3^{+++}$. The ferrous complex is decomposed slowly by strong acids or by salts of Co^{++}, Cu^{++}, Ni^{++}, Zn^{++}, or Cd^{++} which also form complexes with phenanthroline. The blue oxidized form resists further oxidizing action. The color change of red to blue is reversible. To prepare the indicator solution dissolve 1.48 g of o-phenanthroline in 100 ml of 0.025 N ferrous sulfate solution. The indicator can also be purchased under the name *Ferroin*. The color change takes place when 90 per cent of the indicator has been oxidized and the oxidation potential is about 1.20 volts, which is much higher than in the case of the above-mentioned indicators. This indicator is very useful in titrations with ceric sulfate of solutions containing ferrous iron, ferrocyanide, vanadyl salt, etc., but with dichromate titrations the diphenylamine sulfonate is better. The present cost of o-phenanthroline is about $2.00 a gram.

REDUCTION METHODS

1. Determination of Ferric Iron (Fresenius)[1]

Strictly speaking, all the iodimetric methods in which a reduction is accomplished with potassium iodide and acid, are reduction methods.

In methods thus far discussed, except in iodimetry, it was necessary to reduce the iron to the ferrous condition before it could be determined volumetrically. In the following method, first suggested by Penny and Wallace,[2] but improved by Fresenius, the iron in the *ferric* condition may be determined with accuracy and rapidity.

The hydrochloric acid solution containing ferric chloride is titrated hot with stannous chloride solution until the former becomes colorless. By this means the ferric salt is reduced to ferrous salt:

$$2FeCl_3 + SnCl_2 = SnCl_4 + 2FeCl_2$$

Inasmuch as it is not very easy to determine the end point with accuracy, because the last part of the iron is reduced very slowly, it is customary to run over the end point and to titrate the excess of the stannous chloride with iodine solution.

Solutions Required. 1. *A Ferric Chloride Solution Containing a Known Amount of Iron.* Dissolve exactly 10.03 g of pure iron wire in 150 ml of 6 N hydrochloric acid in a long-necked flask held in an inclined position; oxidize the iron with potassium chlorate, and boil off the excess of chlorine. Transfer the ferric chloride solution to a liter flask and dilute to the mark with water; 50 ml of this solution contains 0 5 g of pure iron[3]

2. *A Stannous Chloride Solution.* Heat 25 g of tinfoil in a covered porcelain dish for 2 hours on the water bath with 50 ml of 8 N hydrochloric acid and a few drops of chloroplatinic acid to form a **Pt-Sn** couple which helps dissolve the tin. Add 150 ml more of hydrochloric acid and an equal volume of water, filter, and dilute to 1 l. As stannous chloride is oxidized by contact with the air, keep the solution in a flask which on one side is connected with the buret as shown in Fig. 81, p. 485, and on the other side with a **Kipp** carbon dioxide generator.

3. *An Iodine Solution, Approximately Tenth-Normal.*

[1] *Z. anal. Chem* , 1, 26.
[2] *Dinglers Polytech. J* , 149, 440.
[3] The assumption being made that the iron wire contained 99.7 per cent pure iron.

(a) *Standardization of the Solutions.* First titrate the stannous chloride and iodine solutions against each other. Measure out 2 ml of the former with a pipet, dilute to about 60 ml, add a little starch solution, and titrate the mixture with iodine until a blue color is obtained.

Next, titrate 50 ml of the acid ferric chloride solution against the stannous chloride solution.

(b) *Determination of Iron in Hematite.* Roast 5 g of the finely divided ore at a dull red heat to destroy any organic matter which may be present, place the powder in a long-necked flask, and heat with 25 ml of concentrated hydrochloric acid and a little potassium chlorate until all the iron oxide is dissolved, leaving a white sandy residue. Add 20 ml more of hydrochloric acid and continue the boiling, while passing a current of air through the solution, until all the excess of chlorine is completely removed and the escaping vapors will no longer set free iodine when passed into a potassium iodide solution. Dilute the solution thus obtained to exactly 500 ml and use 50 ml for the analysis.

Example

1. *Standardization of the Reagents·*

2 ml of stannous chloride solution requires 7.2 ml of iodine solution. 1 ml iodine solution..	= 0.278 ml SnCl₂

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solution. 1 ml iodine solution.. .... $= 0.278$ ml $SnCl_2$

50 ml ferric chloride solution ($= 0.5$ g iron) requires for decolorization.................... 30.34 ml $SbCl_2$

and for the titration of the excess 0.51 ml of iodine solution
$= 0.51 \times 0.28$. $\underline{\quad 0.14 \text{ ml } SnCl_2}$

Consequently, 50 ml ferric chloride solution $= 0.5$ g iron .... $= 30.20$ ml $SnCl_2$

and 1 ml $SnCl_2 = \dfrac{0.5}{30.20} = 0.01656$ g Fe.

2. *Titration of the Solution to Be Analyzed:*

50 ml ($= 0.5$ g of iron ore) requires. .... 18.96 ml $SnCl_2$

and for the titration of the excess 0.64 ml of iodine $= 0.64 \times 0.28$. .... $\underline{\quad 0.18 \text{ ml } SnCl_2}$

so that 0.5 g of ore corresponds to........ .... 18.78 ml $SnCl_2$

and contains, therefore, $18.78 \times 0.01656 = 0.3110$ g Fe...... $= 62.20\%$ Fe

2. Determination of Tin by Ferric Chloride[1]

This method is suitable for determining tin in tin-plating baths. It is included here because it is the reverse of the procedure just described.

Principle. When a ferric chloride solution is added to a solution containing stannous chloride it is decolorized, then a pale greenish ferrous solution is obtained,

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[1] Method of O. Meister.

CHAPTER XVI

REDUCTION METHODS

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In methods thus far discussed, except in iodimetry, it was necessary to reduce the iron to the ferrous condition before it could be determined volumetrically. In the following method, first suggested by Penny and Wallace,[2] but improved by Fresenius, the iron in the *ferric* condition may be determined with accuracy and rapidity.

The hydrochloric acid solution containing ferric chloride is titrated hot with stannous chloride solution until the former becomes colorless. By this means the ferric salt is reduced to ferrous salt:

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2. *A Stannous Chloride Solution.* Heat 25 g of tinfoil in a covered porcelain dish for 2 hours on the water bath with 50 ml of 8 N hydrochloric acid and a few drops of chloroplatinic acid to form a Pt-Sn couple which helps dissolve the tin. Add 150 ml more of hydrochloric acid and an equal volume of water, filter, and dilute to 1 l. As stannous chloride is oxidized by contact with the air, keep the solution in a flask which on one side is connected with the buret as shown in Fig. 81, p. 485, and on the other side with a Kipp carbon dioxide generator.

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(b) *Determination of Iron in Hematite.* Roast 5 g of the finely divided ore at a dull red heat to destroy any organic matter which may be present, place the powder in a long-necked flask, and heat with 25 ml of concentrated hydrochloric acid and a little potassium chlorate until all the iron oxide is dissolved, leaving a white sandy residue. Add 20 ml more of hydrochloric acid and continue the boiling, while passing a current of air through the solution, until all the excess of chlorine is completely removed and the escaping vapors will no longer set free iodine when passed into a potassium iodide solution. Dilute the solution thus obtained to exactly 500 ml and use 50 ml for the analysis.

Example

1. *Standardization of the Reagents·*

2 ml of stannous chloride solution requires 7.2 ml of iodine solution. 1 ml iodine solution....................	= 0.278 ml SnCl₂
50 ml ferric chloride solution (= 0.5 g iron) requires for decolorization....................................	30.34 ml SbCl₂
and for the titration of the excess 0.51 ml of iodine solution = 0 51 × 0.28S..............................	0.14 ml SnCl₂
Consequently, 50 ml ferric chloride solution = 0.5 g iron	= 30.20 ml SnCl₂

and 1 ml SnCl₂ = $\frac{0.5}{30.20}$ = 0 01656 g Fe.

2. *Titration of the Solution to Be Analyzed:*

50 ml (= 0 5 g of iron ore) requires.	18 96 ml SnCl₂
and for the titration of the excess, 0 64 ml of iodine = 0 64 × 0.2S	0.18 ml SnCl₂
so that 0 5 g of ore corresponds to........................	18.78 ml SnCl₂

and contains, therefore, 18.78 × 0 01656 = 0 3110 g Fe...... = 62.20% Fe

2. Determination of Tin by Ferric Chloride[1]

This method is suitable for determining tin in tin-plating baths. It is included here because it is the reverse of the procedure just described.

Principle. When a ferric chloride solution is added to a solution containing stannous chloride it is decolorized, then a pale greenish ferrous solution is obtained,

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[1] Method of O. Meister.

and finally, when an excess of ferric chloride is present, a yellowish tint is easily recognized as the end point. If, when the titration is made in this way, so much pale green ferrous salt is formed that the end point is hard to recognize, this difficulty can be overcome by first oxidizing the greater part of the tin with normal potassium chlorate solution.

$$SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2$$

$$3SnCl_2 + KClO_3 + 6HCl = 3H_2O + KCl + 3SnCl_4$$
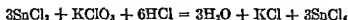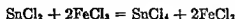
Requirements. 1. Normal potassium chlorate solution. Dissolve 20.43 g of pure potassium chlorate, dried at 120°, in a little water and dilute with water at 20° to 1 l.

2. Normal ferric chloride solution. Dissolve 56 g of pure iron in 600 ml of 6 N hydrochloric acid. Heat toward the last, and gradually introduce 20 g of potassium chlorate. Boil till all the excess chlorine is removed, dilute to about 900 ml, filter if necessary, and dilute to exactly 1 l at 20°.

Standardization of the Ferric Chloride Solution and Simultaneous Determination of the Tin Content of a Solution. Transfer 25 ml of the tin solution, which should contain about 30 g of tin in 300 ml of 6 N hydrochloric acid, into a 200-ml flask held in an inclined position. Add 0.3 g of aluminum powder, which will cause the precipitation of metallic tin. After the evolution of hydrogen ceases, add 20 ml of concentrated hydrochloric acid, place a small funnel in the neck of the flask, and heat till all the tin is dissolved again. Rinse out the funnel and the neck of the flask with hot water and run in ferric chloride solution from a buret into the boiling solution until the greenish yellow end point is obtained. Call the volume of ferric chloride solution T.

Reduce another portion of the tin solution in exactly the same way but instead of adding ferric chloride solution, first oxidize the greater part of the tin with t ml of N potassium chlorate solution and finish with t_1 ml of the ferric chloride solution. Evidently $T - t_1$ ml of the ferric chloride solution is equivalent to t ml of N potassium chlorate solution and 1 ml of $FeCl_3$ solution $= \dfrac{t}{T - t_1} = f$ ml of N solution $= f \times 0.05935$ g of Sn. The tin content of the original solution is then

$$\frac{T \times f \times 59.35}{25} \text{ g Sn per liter}$$

3. Determination of Ferric Iron by Means of Titanous Chloride
(Knecht and Hibbert)[1]

$$1000 \text{ ml of } 0.1 \ N \text{ TiCl}_3 \text{ solution} = \frac{Fe}{10} = 5.585 \text{ g Fe}$$

Principle. If an acid solution of a ferric salt is treated with titanous chloride, the iron is immediately reduced in the cold to the ferrous condition:

$$FeCl_3 + TiCl_3 = TiCl_4 + FeCl_2$$

Preparation of Titanous Chloride Solution. A concentrated solution of titanous chloride, prepared by the electrolysis of $TiCl_4$, can now be obtained on the market. To such a solution add an equal volume of concentrated hydrochloric acid, boil to expel any hydrogen sulfide, and dilute with 10 times as much boiled water.

Preserve the solution in contact with an atmosphere of hydrogen, or carbon dioxide, in a bottle such as is shown in Fig. 81, p. 485, which is connected with a buret, and in this case with a Kipp hydrogen, or carbon dioxide, generator instead of the soda-lime tube.

Standardization of the Titanous Chloride Solution. Prepare a ferric chloride solution of known strength as described on p. 640, and of this solution measure out 50 ml into a beaker, and slowly add the titanium trichloride with constant stirring, while a current of carbon dioxide is being constantly passed into the beaker. After the solution is nearly decolorized, introduce a drop of potassium thiocyanate solution, and continue the adding of titanous chloride to the disappearance of the red color.

The analysis proper is carried out in exactly the same manner.

4. Determination of Ferrous and Ferric Iron by the Titanium Method

First titrate the ferrous iron with permanganate in the presence of manganous sulfate (cf. p. 545), and then determine the total iron with titanous chloride.

The method can be carried out very rapidly, and the results are accurate.

5. Determination of Hydrogen Peroxide[2]

If titanous chloride is run into an acid solution of hydrogen peroxide, the latter is colored first yellow, then a deep orange, and as soon as the

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[1] *Ber.*, **36**, 1551 (1903). $TiCl_3$ is a very efficient reducing agent and has been used for many determinations. Cf. Knecht and Hibbert, *New Reduction Methods in Volumetric Analysis*, Longmans, Green & Co.

[2] Knecht and Hibbert, *loc. cit.*

maximum depth of color is produced, it begins to fade upon the further addition of titanous chloride until finally the solution becomes colorless, which is taken as the end point.

The reaction takes place in two stages:

$$2TiCl_3 + 3H_2O_2 + 2H_2O = 2H_2TiO_4 + 6HCl$$

$$H_2TiO_4 + 2TiCl_3 + 6HCl = 3TiCl_4 + 4H_2O$$
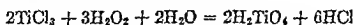
or combining the two equations:

$$2TiCl_3 + H_2O_2 + 2HCl = 2TiCl_4 + 2H_2O$$

On account of the fact that the reducing value of the titanous chloride solution is not very permanent, it should be standardized against ferric chloride before each series of experiments.

If t ml of titanous chloride solution of which 1 ml $= \alpha$ g Fe was required for the reduction of 1 ml of hydrogen peroxide, then

$$\frac{34.02 \times \alpha t}{111.7} \text{ g } H_2O_2 \text{ is present} = 30.46 \text{ } \alpha t \text{ per cent } H_2O_2$$

If it is desired to express the percentage in percentage by volume of active oxygen (cf. p. 562) the following equation holds:

$$10030 \cdot \alpha t = \text{per cent oxygen by volume}$$

According to Knecht and Hibbert,[1] persulfuric acid may likewise be estimated by titration with titanous chloride. The solution of the persulfate is treated with titanous chloride solution, and the excess of the latter is titrated with ferric chloride in an atmosphere of carbon dioxide.

6. Determination of Hypochlorous Acid by Means of Arsenious Acid

1 l of 0.1 N Na_3HAsO_3 solution $= 3.546$ g chlorine

(a) Method of Penot[2]

On adding an arsenite to a solution of a hypochlorite, the former is oxidized to arsenic acid, while the latter is reduced to chloride:

$$HAsO_3^{--} + ClO^- = HAsO_4^{--} + Cl^-$$

The end point is reached when a drop of the solution added to a piece of iodo-starch paper will cause no blue coloration.

Alkali hypochlorites and chloride of lime may be analyzed by this method, and the results obtained are more reliable than those obtained

[1] Knecht and Hibbert, Ber., 38, 3324 (1905).
[2] J. prakt. Chem., 54, 59 (1851).

by the iodimetric method described on p. 601, for the presence of chlorate has no effect in this case.

(b) Method of Pontius

1 l of 0.1 N KI solution = 2.767 g KI = 3.546 g of chlorine

This method is useful for the determination of the available chlorine in bleaching powder and depends upon the fact that potassium iodide is immediately oxidized to iodate by contact with bleaching powder in the presence of sodium bicarbonate solution.

$$3CaOCl_2 + KI = KIO_3 + 3CaCl_2$$
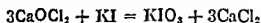
If potassium iodide solution is added to sodium bicarbonate solution containing bleaching powder and starch paste, a permanent blue color will not be obtained until all the bleaching powder has been decomposed. Then free iodine is formed and the end point is reached.

$$IO_3^- + 5I^- + 6Ca^{++} + 6HCO_3^- \rightarrow 6CaCO_3 + 3H_2O + 3I_2$$
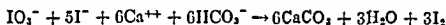
From these equations it is clear that in this procedure the normal solution of potassium iodide contains only ⅙ mole of the salt instead of 1 mole.

Procedure. Triturate 7.092 g of chloride of lime in a porcelain mortar with a little water, rinse into a liter measuring flask, and fill to the mark with water. Mix thoroughly and without allowing any of the precipitate to settle, transfer with a pipet 50 ml of the liquid to a beaker, add 3 g of sodium bicarbonate, and titrate with $N/10$ potassium iodide until a permanent blue is obtained with starch paste as indicator. In this case the volume of iodide used is the same as the percentage of available chlorine in the sample.

Remark. Pontius recommends standardizing the potassium iodide solution as follows: Titrate 50 ml of the chloride of lime suspension as above and another portion with 0.1 N arsenite solution by the preceding method of Penot.
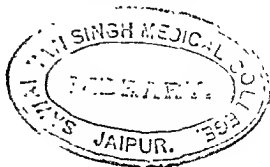
CHAPTER XVII

PRECIPITATION METHODS

1. Determination of Silver. Method of Gay-Lussac

This exceedingly accurate determination, which is extensively used for testing silver alloys, depends upon the precipitation of silver chloride from nitric acid solution. Common salt is used as the precipitant.

Solutions Required. 1. *Sodium Chloride Solution of Known Concentration.* For convenience, it is customary to make the solution of such a strength that 1000 ml corresponds to exactly 5 g of silver. To help in getting the end point, however, 0.1 per cent less than the theoretical quantity is used. Weigh out 2.710 g of chemically pure salt, dissolve in distilled water, and dilute to 1 l at 20°.

2. *Decimal Solution of Sodium Chloride.* Dilute 100 ml of the above solution with distilled water to 1 l.

In laboratories where silver determinations are frequently made, the above solutions are made up in much larger quantities and kept in bottles similar to the one shown in Fig 81, p. 485. For the stronger solution use a 100-ml pipet and connect the decimal solution with a buret.

Standardization of the Sodium Chloride Solution. Weigh out exactly 0.5 g of chemically pure silver into a 200-ml flask provided with a well-ground glass stopper, and dissolve in 10 ml of 6 N nitric acid, free from chlorine. Hasten the dissolving by heating on a sand bath. When the silver has dissolved, heat the solution to boiling to expel the nitrous acid formed. Remove the brown vapors by blowing air into the flask. As soon as no more of these are formed, remove the flask from the sand bath and allow to cool. To the silver solution add exactly 100 ml of the stronger salt solution, stopper the flask, and shake vigorously until the precipitated silver chloride collects together, and the supernatant liquid appears clear.

As the salt solution was made up a little weak, the precipitation of the silver is not quite complete and consequently more sodium chloride must be added. For this purpose add half a milliliter of the decimal salt solution from the buret, so that the solution runs down the sides of the flask upon the surface of the liquid, causing a distinct cloud of silver chloride to be formed. Shake the liquid, allow the precipitate to settle, again treat with half a milliliter of the decimal salt solution, and repeat the process until finally the addition of the salt solution fails

to produce any further turbidity; the last half cubic centimeter is not used in the calculation.

Example. 0.5 g of chemically pure silver (§§§§ fine) required 100 ml of the standard salt solution + 1 ml of the decimal solution, i.e., 100.1 ml of the salt solution corresponds to 1000 silver;[1] this is the value of the salt solution.

Silver Determination. To obtain absolutely accurate results it is necessary to employ the same amount of silver for the analysis as was used in the standardization of the solution; consequently the approximate amount of silver present in the alloy must be determined. This can be accomplished by cupellation, or volumetrically by the method of Volhard, described further on.

Example. It was found by cupellation that an alloy contained about $\frac{800}{1000}$ fine silver; for the titration an amount must be taken which will contain 0.5 g of silver; we have then, $0.5/0.8 = 0.625$ g.

Weigh out, therefore, 0.625 g (= 1250) of the alloy[2] and proceed exactly as in the standardization.

For the precipitation of the silver, 1250 parts of alloy requires 100 ml of the standard salt solution + 3 ml of the decimal solution, i.e., 1250 parts of the alloy requires 100.3 ml of the standard salt solution. Since 100.1 ml of this salt solution corresponds to 1000 parts of pure silver, there must $\dfrac{1000 \times 100.3}{100.1} = 1002$ parts silver in 1250 parts of alloy;

so that in 1000 parts of the alloy there will be $\dfrac{1002 \times 1000}{1250} = 801.6$ parts of silver.

This procedure is designated as the French method in contrast to the German or Dutch method. In the latter case, 0.5 g of the alloy (= 100) is weighed out and the same amount of silver is added which the alloy lacks in fineness. In this way one more weighing is necessary, but the calculation is somewhat simpler.

Example. By cupellation an alloy is found to contain $\frac{800}{1000}$ silver. In order to make the silver equal 1000, 200 parts of fine silver must be added. For the analysis, therefore, 0.5 g of the alloy and 0.1 g of pure silver (= 200) are taken dissolved in nitric acid, and titrated with sodium chloride

2. Determination of Silver. Method of Volhard

$$1 \, l \text{ of } 0.1 \, N \text{ KCNS} = \frac{Ag}{10} = 10.79 \, g \, Ag$$

If alkali thiocyanate is added to a solution containing both silver and

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[1] For convenience in calculation, 0.5 g of pure silver is designated by 1000, 0.25 g by 500, and 0.1 g by 250, etc.

[2] If 0.5 g = 1000, then $0.5 : 1000 = 0.625 : x$; $x = 1250$.

ferric ions, white, insoluble silver thiocyanate will form preferably and a *permanent* red coloration of ferric thiocyanate will not be obtained until practically all silver is precipitated:

$$CNS^- + Ag^+ \rightarrow AgCNS$$

$$3CNS^- + Fe^{+++} \rightarrow [Fe(CNS)_3]$$
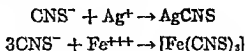
Requirements. 1. *Tenth-Normal Potassium (or Ammonium) Thiocyanate Solution.* As both these salts are hygroscopic and cannot be dried without decomposition, an exactly tenth-normal solution cannot be prepared by weighing out the solid salt. Dissolve approximately the right amount (about 10 g KCNS or 9 g NH_4CNS) in a liter of water.

2. *Ferric-Ammonium Alum Solution.* A cold, saturated solution of ferric alum to which enough nitric acid is added to cause the disappearance of the brown color. Use about 3.5 g of the alum, 10 ml of water, and 2 ml of 6 N HNO_3. Of this indicator use the same amount for all titrations, about 2–3 ml for 100 ml of the silver solution.

Standardization of Thiocyanate Solution

Weigh out portions of about 0.4 g of pure silver nitrate and dissolve in 100 ml of 0.3 N nitric acid. Add 2–3 ml of indicator solution and titrate with thiocyanate solution to a permanent red tint in the solution. Or dissolve 0.25-g portions of pure silver in 15 ml of 6 N nitric acid. Dilute to about 25 ml, boil till all nitrous fumes are expelled, add 75 ml of cold water and the indicator solution, and titrate with thiocyanate.

Determination of Silver in Silver Alloys

Dissolve 0.5 g of the brightly polished metal in 10 ml of 6 N nitric acid. After the silver has dissolved, dilute with 50 ml of water and boil to expel nitrous fumes.[1] Cool, add 2–3 ml of the ferric alum solution, and titrate with the thiocyanate solution as in the standardization. The presence of metals whose salts are colorless does not influence the accuracy of this determination, except that mercury must be absent because its thiocyanates are insoluble. Nickel and cobalt must not be present to any extent, because their salts are colored, and not more than 60 per cent of copper in an alloy is permissible. If more copper is present the following procedure must be used: Precipitate the silver by means of an excess of alkali thiocyanate, wash completely with water, place the funnel over an Erlenmeyer flask, break the apex of the filter,

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[1] Nitrous acid reacts with thiocyanic acid, forming a red compound which may easily be mistaken for ferric thiocyanate.

wash its contents into a flask by means of concentrated nitric acid, and heat the liquid to gentle boiling for three-quarters of an hour. As the sulfuric acid formed will have some effect upon the subsequent titration, dilute the solution with water to about 100 ml, and add a concentrated barium nitrate solution, drop by drop, until all the sulfuric acid is precipitated. Then titrate the silver with the thiocyanate solution without filtering off the barium sulfate.

3. Determination of Mercury

Mercuric thiocyanate, like silver thiocyanate, is so insoluble that the nitrate or sulfate solution can be titrated with standard thiocyanate solution using ferric alum as indicator. The method fails, however, when chloride is present because mercuric chloride is so slightly ionized that it does not react completely. This constitutes the principal reason why the method is not used in preference to other methods, because hydrochloric acid is commonly used in dissolving the sample and the complete removal of chloride without volatilization of any mercuric chloride is difficult. The titration gives excellent results in a nitrate or sulfate solution and can be carried out in the presence of lead, copper, bismuth, cadmium, tin, arsenic, antimony, thallium, iron, zinc, manganese, nickel, and cobalt. Mercurous salt, silver, and nitrous acid should be absent.

Procedure. To the solution containing 0.05 to 0.3 g of mercury as sulfate or nitrate in a volume of about 100 ml, add nitric or sulfuric acid sufficient to make the solution about 1.5 N in acid and, to make sure of the absence of nitrous acid or mercurous iron, add 5 per cent permanganate solution dropwise until a red color is produced, or a manganese dioxide precipitate is formed, which persists for 5 minutes. Destroy the excess permanganate, or dissolve the precipitate, by the addition of a very little ferrous sulfate or hydrogen peroxide. Titrate as described for the determination of silver but, as the color of ferric thiocyanate is noticeable before the end of the titration and disappears very slowly at the last, make sure that the solution is not under-titrated and that distinct red color persists after vigorous shaking or stirring.

Prepare the standard solution of thiocyanate and the indicator solution of ferric alum as described under the determination of silver. It is best, however, to standardize the solution of thiocyanate by direct titration against 0.25-0.30 g of mercury that has been dissolved in hot 6 N nitric acid and titrated under the conditions outlined above.

4. Determination of Chloride

(a) Volhard's Method

$$1 \; l \text{ of } 0.1 \; N \; AgNO_3 \text{ solution} = \frac{Cl}{10} = 3.546 \text{ g chlorine}$$

According to Volhard's original directions, the chloride solution was treated with 0.1 N silver nitrate solution and then, without filtering off the precipitate, 2–3 ml of the ferric-ammonium alum solution was added and the excess of silver titrated with 0.1 N potassium or ammonium thiocyanate (see p. 648).

The results are satisfactory with large quantities of chloride, but in the titration of small quantities of chloride too high results are obtained, as was first shown by G. Drechsel[1] and later confirmed by M. A. Rosanoff and A. E. Hill.[2] Drechsel showed that it was impossible to get the true end point of the reaction, as the red coloration gradually disappeared on stirring, remaining permanent only after a considerable excess of thiocyanate had been added. The reason for this is that silver chloride is more soluble than silver thiocyanate. Thus the precipitate gradually reacts with the red ferric thiocyanate, as follows:

$$3AgCl + Fe(CNS)_3 = 3AgCNS + FeCl_3$$
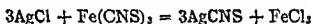
Procedure. Weigh out accurately to four significant figures samples of about 0.2 g each. Dissolve in about 200 ml of water containing 5 ml of 6 N HNO$_3$. In other beakers, dissolve about 0.8-g portions of pure AgNO$_3$, also weighed to four significant figures. Dissolve the AgNO$_3$ in about 50 ml of hot water and pour the silver nitrate solution slowly, while stirring, into the hot chloride solution. Wash the beakers well to remove all AgNO$_3$. Keep the solutions hot, but not quite boiling, until the silver chloride precipitate has coagulated sufficiently to be filtered. Filter off the precipitate, and wash the beakers and precipitate with at least 6 portions of hot water. In washing the precipitate on the filter, make sure that the upper edge of the paper is washed each time; if the filter paper fits the funnel tightly at the top, no precipitate will pass into the filtrate. Finally, to make sure that all the excess silver nitrate has been removed, test about 5 ml of fresh filtrate with a few drops of 6 N HCl; no precipitate of AgCl should form. Add ferric alum indicator solution and titrate with standardized thiocyanate solution.

[1] *Z. anal. Chem.*, **16**, 351 (1877).

[2] *J. Am. Chem. Soc.*, **29**, 269.

The above procedure is equally applicable to the analysis of bromides, iodides, cyanides, and thiocyanates, all of which yield precipitates insoluble in dilute HNO_3. When the above procedure is followed it is not absolutely necessary to filter off the precipitate before titrating. The error is slight if the silver chloride precipitate is well coagulated.

Adsorption Indicators. Fajans and his collaborators[1] have shown that silver halide precipitates, owing to their colloidal properties, tend to adsorb excess Ag^+ or excess halogen ions from the solution with which they are in contact. The adsorbed Ag^+ has the property of dragging down with it the anions of certain organic dyestuffs, which are of a feebly acidic nature, and a change of color takes place as a result of the adsorption. Thus fluorescein in aqueous solution has a yellowish green color. When silver chloride is formed in the presence of a very slight excess of Ag^+, the anion of fluorescein is adsorbed and there is a change of color to reddish violet. If a very little of the indicator is present, the silver chloride precipitate assumes a reddish tint as soon as a very slight excess of Ag^+ is present.

In the titration of Cl^- with Ag good results are thus obtained in neutral solutions with fluorescein as indicator. To prepare the indicator solution, dissolve 0.2 g of the sodium salt of fluorescein in 100 ml of water or dissolve 0 2 g of fluorescein itself in 100 ml of alcohol. Use about 2 drops of indicator solution for each 10 ml of 0.1 N chloride solution to be titrated with 0 1 N silver nitrate solution. The results are accurate, even in the presence of considerable quantities of alkali cations, provided that the chloride solution is at least 0 005 N in halogen ions. Alkaline-earth cations interfere somewhat.

Bromides, iodides, and thiocyanates can be titrated in dilute solutions, even in the presence of dilute nitric acid, when eosin is chosen as the indicator. Two drops of the 0 5 per cent aqueous solution should be used for each 10 ml of 0.1 N halide to be titrated. The silver halide precipitate becomes red at the end point. Eosin cannot be used for the titration of chlorides with silver nitrate because the eosin is adsorbed and colors the silver chloride precipitate before the end point is reached. Fluorescein, on the other hand, can be used with chlorides, bromides, iodides, or thiocyanates.

In the titration of silver solutions, there are two ways in which an adsorption indicator can be used An excess of standard halide solution can be added and the excess titrated with standard silver nitrate solution using fluorescein or eosin as indicator, or a slightly basic indicator can be used such as "rhodamine 6 G." In this case the cations of the indicator are adsorbed by the precipitate as soon as a slight excess of Br^- has been added and a color change takes place with the precipitate assuming a bluish violet hue. Nitric acid can be present during this titration with the basic indicator provided that the concentration is not over 0.5 N in acid.

A number of other organic dyestuffs can be used as adsorption indicators. Thus Kolthoff[2] reports geⸯ   and metanil yellow

[1] *Z. physik. Chem.*, 97, 478 (1921); 105, 255 (1923); *Z. Electrochem.*, 29, 495 (1923); *Naturwiss.*, 11, 165 (1923); *Z. anorg. allgem. Chem.*, 137, 221 (1924).

[2] *Z. anal. Chem.*, 71, 235 (1927).

A Partial List of Adsorption Indicators for Volumetric Precipitations*

Titration of	Titrating Ion	Indicator	Notes
Cl⁻	Ag⁺	Dichlorofluorescein	$pH > 4$
Br⁻	Ag⁺	Eosin	$pH > 2$ Best in acetic acid solution
I⁻	Ag⁺	Eosin	⎰Eosin is tetrabromo-
SCN⁻	Ag⁺	Eosin	⎱ fluorescein
CN⁻	Ag⁺	Diphenylcarbazide	
Ag⁺	Br⁻	Rhodamine 6 G	In 0.5 N HNO₃
OH⁻	Ph⁺⁺	Fluorescein	Quite sharp in 0.01 and 0.1 N solutions
BO₂⁻ ⎱ B₄O₇⁼ ⎰	Pb⁺⁺	Dichlorofluorescein	Accurate in neutral solution
SO₄⁼	Pb⁺⁺	Dibromofluorescein	A better method is based on fractional precipitation†

* Pierce and Haenisch, *Quantitative Analysis*

† See W. C. Schroeder, *Ind. Eng. Chem*, *Anal Ed*, **5**, 403 (1933), and Sheen, Kahler, and Cline, *ibid*, **9**, 69 (1937).

(b) Fr. Mohr's Method

If the neutral solution of an alkali chloride containing a few drops of potassium chromate solution is treated with silver nitrate solution, added from a buret, silver chloride is formed first, and any red precipitate of silver chromate disappears on stirring, on account of its reacting with chloride ions to form less soluble silver chloride.

$$Ag_2CrO_4 + 2NaCl = 2AgCl + Na_2CrO_4$$

When all the chloride is changed to insoluble silver chloride, the next drop of the silver solution will impart a permanent reddish color to the liquid. For small amounts of chloride in concentrated solutions this method gives very sharp results. If, however, the volume of the solution is too large, the results are not very accurate. A blank experiment must always be made to see how much of the silver solution is necessary to produce the red shade used in the titration when no chloride is present, and this amount must be deducted from that used in the analysis.

Remark. If it is desired to titrate free hydrochloric acid, first neutralize the solution. With colorless chlorides having an acid reaction (AlCl₃), treat the solution with an excess of neutral sodium acetate solution and then titrate. With colored metal chlorides, precipitate the metal with caustic potash or sodium

carbonate, filter, wash the precipitate, make the filtrate acid with acetic acid, and then titrate.

The above procedure can be used equally well for the titration of bromide. The same is true of the Volhard method.

5. Determination of Iodide

Volhard's Method

$$1 \text{ l of } 0.1 \text{ } N \text{ AgNO}_3 \text{ solution} = \frac{I}{10} = 12\,69 \text{ g iodine}$$

If silver iodide is produced in a solution of an iodide by the addition of silver nitrate, the precipitate will usually enclose a measurable amount of either the soluble iodide or the silver nitrate, so that the analysis cannot be accomplished in the same way as in the analysis of chlorides and bromides.

Place the solution in a glass-stoppered flask, dilute to 200–300 ml, and add the silver solution with vigorous shaking until the yellow precipitate collects together and the supernatant liquid appears colorless. As long as the solution appears milky the precipitation is not complete. Finally add a little more silver nitrate and again shake to precipitate any iodide in the pores of the silver iodide. Then add ferric alum solution, titrate the excess of silver with potassium thiocyanate, and calculate the iodine from the amount of silver used. In this way Volhard obtained exact results.

The ferric solution must not be added before the iodine is completely precipitated, because in acid solution it oxidizes the hydriodic acid with separation of iodine. Silver iodide, however, is without action on ferric salts.

6. Determination of Cyanide. Method of Liebig

$$1 \text{ l of } 0.1 \text{ } N \text{ AgNO}_3 \text{ solution} = \frac{KCN}{5} = 13\,02 \text{ g KCN}$$

On adding silver nitrate solution, drop by drop, to a neutral or alkaline solution of an alkali cyanide, a white precipitate is formed when the two liquids first come in contact with one another, but on stirring it redissolves owing to the formation of potassium silver cyanide:

$$AgCN + CN^- \rightarrow [Ag(CN)_2]^-$$
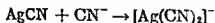
As soon as all the cyanide is transformed into the silver cyanide complex anion, the next drop of the silver solution will produce a permanent turbidity:

$$[Ag(CN)_2]^- + Ag^+ \rightarrow 2AgCN$$
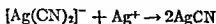
The titration reaction is, therefore,

$$2CN^- + Ag^+ \rightarrow [Ag(CN)_2]^-$$
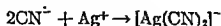
$1Ag^+$ corresponds to $2CN^-$, and the end point of the reaction is shown by the formation of a permanent precipitate as soon as more than $1Ag^+$ has been added for each $2CN^-$ ions.

Prepare the alkali cyanide solution in a beaker, add a little potassium hydroxide, and dilute to a volume of about 100 ml. Place the beaker on a piece of black glazed paper and titrate with constant stirring until the turbidity is obtained.

For the analysis of free hydrocyanic acid, add an excess of potassium hydroxide solution and treat as above.

The addition of 5 ml of 2 per cent potassium iodide solution slightly increases the sharpness of the end point in the above analysis. The precipitate then consists of silver iodide of which 1 molecule will dissolve in 2 molecules of potassium cyanide, just as silver nitrate does. The above procedure can be applied to any solution of alkali or alkaline-earth cyanide (the so-called *free cyanide*) but not to insoluble or complex cyanides.

7. Determination of Chloride and Cyanide in the Presence of One Another

First, determine the cyanide by the method of Liebig, and then add enough silver solution to convert all the cyanide and chloride into their silver salts. Make the solution acid with nitric acid, dilute with water to a definite volume, filter through a dry filter, and after rejecting the first runnings, use an aliquot part of the filtrate for the titration of the excess of silver by means of potassium thiocyanate, according to Volhard. The calculation of the cyanogen and chlorine is illustrated by the following example:

Ten milliliters of the solution required for the production of a permanent turbidity t ml of $0.1\ N$ silver solution. Then an excess of $0.1\ N$ silver solution was added (bringing the total amount used to T ml). The solution was acidified with nitric acid, diluted to exactly 200 ml, filtered through a dry filter, and after the usual rejection of the first runnings the excess of the silver was titrated in 100 ml of the filtrate; this required t_1 ml of $0.1\ N$ potassium thiocyanate solution. Consequently the amount of cyanogen present is $t \times 0.005202$ g, and the chlorine present amounts to $[T - 2(t + t_1)]0.003546$ g.

8. Determination of Potassium Cyanide in the Presence of Ferrocyanide.   Method of W. D. Treadwell[1]

In this determination the use of potassium iodide is necessary because of the appreciable solubility of silver cyanide in alkali ferrocyanide solution.

Procedure.   To one aliquot part of the solution add 0.1 g of potassium iodide, 2-3 ml of 0.1 N caustic alkali solution or ammonium hydroxide, and titrate in a volume of about 100 ml with 0.1 N silver solution till a turbidity forms.   This gives the KCN content.

To determine the ferrocyanide, remove the cyanide by heating another aliquot part of the original solution under a good hood while introducing a stream of carbon dioxide.   This requires about 30 minutes. Then titrate the ferrocyanide according to the directions on p. 561.

9. Determination of Thiocyanic Acid.   Volhard's Method

$$1 \text{ l of } 0.1 \ N \text{ AgNO}_3 \text{ solution} = \frac{\text{HCNS}}{10} = 5.809 \text{ g HCNS}$$

This is the reverse of the silver determination (p. 617).   Add an excess of 0.1 N silver solution to the solution containing the thiocyanate, and titrate the excess of silver with potassium thiocyanate solution, using ferric alum as indicator.

10. Determination of Thiocyanic and Hydrocyanic Acids in the Presence of One Another

Add enough potassium hydroxide to make the solution neutral, dilute to about 100 ml, and titrate the cyanogen by the method of Liebig (p. 653).   Then, add an excess of silver solution, make acid with nitric acid, and titrate the excess of silver with potassium thiocyanate in an aliquot part of the filtrate.

11. Determination of Chloride, Cyanide, and Thiocyanate in the Presence of One Another

In one portion determine the free cyanide according to Liebig.   To a second portion add an excess of 0.1 N silver solution, make acid with nitric acid, filter, wash the precipitate with water, and titrate the excess of silver in the filtrate according to Volhard.   Pierce the filter containing the precipitate and transfer the latter by means of concentrated nitric acid to a flask and boil for three-quarters of an hour.   By this means the cyanide and thiocyanate of silver go into solution, while the

[1] *Z. anorg. Chem.*, **71**, 219 (1911).

silver chloride remains undissolved. Dilute the solution to about 100 ml, add enough barium nitrate to precipitate the sulfuric acid formed, and titrate the silver corresponding to the cyanide and thiocyanate with potassium thiocyanate without filtering off the silver chloride or barium sulfate.

Computation. If t ml of 0.1 N AgNO₃ were used in the first titration, then $2t$ ml would be needed to precipitate all the cyanide. If T ml of 0.1 N AgNO₃ were required to precipitate all the cyanide, thiocyanate, and chloride, and t_1 ml of 0.1 N KCNS were used in the last titration, then

$$t \times 0.005202 = \text{g CN or } t \times 0.01302 = \text{g KCN}$$

$$(t_1 - 2t) \times 0.005808 = \text{g CNS or } (t_1 - 2t) \times 0.009718 = \text{g KCNS}$$

$$(T - t_1) \times 0.003546 \text{ g} = \text{Cl or } (T - t_1) \times 0.007455 = \text{g KCl}$$

12. Determination of Sulfuric Acid by Benzidine Hydrochloride[1]

$$1 \text{ l of } 0.1 \ N \text{ NaOH} = \frac{\text{H}_2\text{SO}_4}{20} = 4.904 \text{ g H}_2\text{SO}_4$$

Benzidine, $C_{12}H_8(NH_2)_2$, is a weak organic base. It forms stable salts with strong mineral acids, of which the sulfate is characterized by its slight solubility, particularly in water containing hydrochloric acid. The base itself is neutral toward phenolphthalein. The aqueous solutions of benzidine salts undergo hydrolysis and react as if the acid were free:

$$C_{12}H_8(NH_2)_2 \cdot 2HCl + 2OH^- \rightarrow 2Cl^- + C_{12}H_8(NH_2)_2 + 2H_2O$$
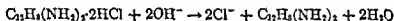
In other words, an aqueous solution of benzidine hydrochloride behaves like a mixture of hydrochloric acid and benzidine, and the amount of acid present may be titrated with alkali hydroxide, in the presence of phenolphthalein as indicator.

There are two methods which have been used for the volumetric estimation of sulfuric acid by means of benzidine. Müller treated the *neutral* solution of the sulfate with a solution of benzidine hydrochloride of known acidity.

$$C_{12}H_8(NH_2)_2 \cdot 2HCl + Na_2SO_4 = 2NaCl + C_{12}H_8(NH_2)_2 \cdot H_2SO_4$$

The precipitate of benzidine sulfate was filtered off and the filtrate titrated with a standard solution of alkali. The loss in acidity corresponded to the amount of sulfuric acid present. Raschig, on the other hand, recommends treating the neutral or acid solution of the sulfate with benzidine hydrochloride solution, filtering off the precipitated benzidine sulfate, washing it, and then suspending it in water and titrating the sulfuric acid with 0.1 N sodium hydroxide at 50°.

Raschig prepares the reagent as follows: Triturate 40 g of benzidine with 40 ml of water and rinse the paste into a liter measuring flask with about 750 ml of water. Add 50 ml of concentrated hydrochloric acid and dilute to the mark. Shake well.

[1] W. Müller, *Ber.*, **35**, 1587 (1902); Müller and Dürkes, *Z. anal. Chem.*, **42**, 477 (1903); F. Raschig, *Z. angew. Chem.*, **1903**, 617 and 818; von Knorre, *Chem. Ind.*, **28**, 2; and Friedheim and Nydegger, *Z. angew. Chem.*, **1907**, 9.

Soon the benzidine will all dissolve, forming a brown solution which may be filtered if necessary. To use as a reagent, dilute with 19 times as much water.

Procedure. To the neutral or slightly acid solution of the sulfate, containing not more than 0.1 g of sulfate anions per 50 ml of solution, add the diluted benzidine solution in the cold, using 150 ml for each 0.1 g of sulfate ions. A crystalline precipitate of benzidine sulfate forms at once, which can be filtered as follows after standing 5 minutes.

Place a Witt perforated porcelain plate in a funnel of 200-ml capacity. The diameter of the plate should be about 40 mm on the top. Place two pieces of filter paper on this plate, about 46 mm in diameter. Insert the funnel in a rubber stopper and place in a suction bottle. Moisten the filters with water, apply gentle suction, and press the papers to the sides of the funnel so that a tight pad is formed of about 3-mm depth, which will not allow precipitate to get by. Pour the supernatant liquid through this filter, rinse the precipitate and mother liquor into the funnel, and drain. Wash with 15 ml of water added in small portions. Place the precipitate and filter, without the porcelain plate, in an Erlenmeyer flask, add 50 ml of water, and shake the contents of the stoppered flask until a homogeneous paste is obtained. Remove the rubber stopper from the flask, rinse off with water, add a drop of phenolphthalein solution, heat to about 50°, and titrate with 0.1 N sodium hydroxide. When the end point is nearly reached, boil the liquid for 5 minutes, and then finish the titration.

Remark. The method does not give good results in the presence of ferric salts, but this difficulty can be overcome by reducing the ferric ion with hydrazine hydrochloride. Not more than 10 moles of HCl, 15 moles HNO$_3$, 20 moles HC$_2$H$_3$O$_2$, 5 moles alkali salt, or 2 moles ferric iron should be present to 1 mole of H$_2$SO$_4$. A satisfactory determination of the sulfur in pyrite can be made by dissolving 0.5 g of the sample according to the Lunge method (see "Pyrite"), evaporating off the nitric acid, taking up the residue in a little hydrochloric acid, diluting to 500 ml and using 100 ml for the treatment with benzidine hydrochloride.

13. Determination of Sulfuric Acid (Hinman)[1]

$$1 \text{ l of 0.1 } N \text{ Na}_2\text{S}_2\text{O}_3 = \frac{\text{H}_2\text{SO}_4}{30} = \frac{98.08}{30} = 3.269 \text{ g H}_2\text{SO}_4$$

This method depends upon the fact that barium chromate is easily dissolved by dilute hydrochloric acid whereas barium sulfate is not; 1 l of cold water dissolves about 2 mg of BaSO$_4$ and 3 mg of BaCrO$_4$, but the latter salt dissolves easily in acid because HCrO$_4^-$ as an acid is comparable to H$_2$CO$_3$. If n solution of barium

[1] *Am. J. Sci. and Arts*, **114**, 478 (1877). Cf. Andrews, *Am. Chem. J.*, **2**, 567; Pennock and Morton, *J. Am. Chem. Soc.*, 1903, 2265; Bruhns, *Z. anal. Chem.*, **45**, 573 (1906). Holliger, *ibid.*, **19**, 84 (1910), and M. Reuter, *Chem. Ztg.*, 1898, 357.

chromate in dilute hydrochloric acid is added in slight excess to a solution containing SO_4^{--} ions, $BaSO_4$ is precipitated; then upon neutralizing the solution the remainder of the barium is precipitated as $BaCrO_4$, leaving 1 mole of CrO_4^{--} in solution for each mole of SO_4^{--} originally present. After filtering, the dissolved chromium can be determined iodimetrically (p. 605).

The method is rapid and capable of giving theoretical values in the analysis of sulfates containing less than 5 per cent of SO_3. By slightly varying the conditions, however, the results are influenced and the most favorable conditions are not always the same for different sulfates. The method, therefore, is suitable for routine work, but is not theoretically perfect.[1]

The results are likely to be high if the barium chromate contains any water-soluble chromate. Since the solubility of barium chromate in hot water is appreciable there will always be a positive error from this source, if the solution is filtered hot.

The results will be low: (1) If there is any reduction of chromate other than the desired reduction with iodide; this may be caused by the presence of too much hydrochloric acid during the first precipitation. (2) If any other chromate is precipitated with the barium chromate, such as basic ferric chromate. (3) If the solution is not acid enough during the treatment with iodide, incomplete reduction may result. (4) If the solution is hot, or contains an insufficient amount of iodide, some loss of the iodine may take place.

Prepare the barium chromate reagent by precipitating barium chloride with potassium chromate at the boiling temperature. Wash the precipitate with hot, dilute acetic acid and then with water till free from chromate. Dissolve 2–4 g of the dry salt in 1 l of normal hydrochloric acid. One milliliter should precipitate 0.63–1.3 mg of SO_4.

Procedure. If the solution of the sulfate is acid, nearly neutralize it with alkali hydroxide solution. Dilute with water until not more than about 5 mg of SO_3 is present in 100 ml. Heat to boiling and slowly add a slight excess of the barium chromate reagent. Boil for 1 minute, or for 5 minutes if any carbonate was present.

To the boiling solution cautiously add pure $CaCO_3$ in small portions until present in slight excess (use ammonia if iron, nickel, or zinc is present). Cool to room temperature and dilute to the mark in a 250-ml measuring flask. Mix thoroughly by pouring back and forth several times into a beaker which is dry at the start, filter through a dry filter, reject the first 20 ml and take 100 ml of the filtrate for the titration.

Add 2–3 g of potassium iodide and 10 ml of concentrated hydrochloric acid. Shake well and allow to stand 15 minutes. Then titrate slowly with 0.02 N sodium thiosulfate solution.

Remark. When iron, nickel, or zinc salts are contained in the solution, the acid present cannot be neutralized with calcium carbonate, because these salts when boiled with calcium carbonate and a soluble chromate form insoluble basic chromates, so that too little chromic acid will be found in the filtrate corresponding to too little

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[1] In some cases it is simplest to apply a correction factor. Thus Komarowsky, *Chem.-Ztg.*, **31**, 498 (1907), deducts 0.3 ml from the final buret reading.

sulfuric acid. In such a case the neutralization is effected with ammonia, an excess being added, the solution boiled until the excess is almost entirely expelled and then filtered.

14. Determination of Phosphoric Acid. Method of Pincus

Principle. If a neutral solution, or one slightly acid with acetic acid, is treated with uranyl acetate, a greenish white precipitate of uranyl phosphate is formed:

$$KH_2PO_4 + UO_2(C_2H_3O_2)_2 = KC_2H_3O_2 + HC_2H_3O_2 + UO_2HPO_4$$

If at the same time ammonium salts are present, ammonium is contained in the precipitate:

$$KH_2PO_4 + UO_2(C_2H_3O_2)_2 + NH_4C_2H_3O_2 =$$
$$KC_2H_3O_2 + 2HC_2H_3O_2 + UO_2NH_4PO_4$$
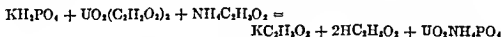
The end of the precipitation can be determined by testing a drop of the solution on a porcelain tile with potassium ferrocyanide. A brown coloration is formed as soon as an excess of uranyl salt has been added.

To precipitate the phosphoric acid completely, it is necessary to titrate in a boiling-hot solution. However, as a solution of calcium phosphate will become turbid on boiling, owing to the formation of secondary calcium phosphate (CaHPO$_4$), it is best to precipitate the greater part of the phosphoric acid in the cold, then heat to boiling and complete the titration.

Requirements. 1. *Potassium Phosphate Solution.* Dissolve 19.23 g (corresponding to 10 g P$_2$O$_5$) of pure monopotassium phosphate in 1 l of water.

Confirm the concentration of the solution by evaporating 50 ml to dryness in a large platinum crucible, igniting the residue over the full flame of a Bunsen burner and weighing as KPO$_3$; also by precipitating another portion as magnesium ammonium phosphate and weighing as magnesium pyrophosphate.

Fifty milliliters of the solution corresponds to 0 5 g P$_2$O$_5$ and should yield 0 8315 g KPO$_3$ and 0 7839 g Mg$_2$P$_2$O$_7$.

2. *Calcium Phosphate Solution.* Dissolve 5.461 g of Ca$_3$(PO$_4$)$_2$, corresponding to 2.5 g P$_2$O$_5$, in a little nitric acid, dilute with water to a volume of 1 l, and test the concentration of the solution by means of the molybdate method (p. 371).

3. *Uranyl Acetate Solution.* Dissolve about 35 g of uranyl acetate in a liter of water

4. *Ammonium Acetate Solution.* Dissolve 100 g of pure ammonium acetate and 100 ml of 6 N acetic acid, in enough water to make 1 l of solution.

5 *Potassium Ferrocyanide.* The salt is used in the powdered form.

Procedure

(a) Standardization of the Uranium Solution

To 50 ml of the potassium phosphate, or calcium phosphate, solution add 10 ml of the ammonium acetate solution; run in the uranyl acetate solution from a buret until a drop of the solution will show a brown coloration when treated with solid potassium ferrocyanide upon a white porcelain tile. Then heat the solution to boiling, when a drop of

it will no longer react with the ferrocyanide. To the hot solution add more of the uranium solution until the brown color is obtained once more.

If, for the precipitation of the phosphoric acid contained in 50 ml of the potassium phosphate solution (0.5 g P_2O_5), T ml of the uranium solution was required, its concentration is $\dfrac{0.5}{T}$ g P_2O_5 per milliliter.

For the analysis of alkali phosphates, standardize the solution against the potassium phosphate solution, but for the analysis of an alkaline-earth phosphate use the solution of calcium phosphate.

(b) Determination of Phosphoric Acid in Alkali Phosphate

The solution to be analyzed should be of about the same concentration as that of the potassium phosphate used for the standardization, and titrated in the same way. Phosphate solutions of different concentrations give different results by the titration.

(c) Determination of Phosphoric Acid in Calcium Phosphate

Dissolve 0.25 g of calcium phosphate in dilute nitric acid, add ammonia until a permanent precipitate is produced, and redissolve this in a little acetic acid. Add 10 ml of the ammonium acetate solution, and titrate the solution with the standard solution of uranyl acetate.

Remark. In the presence of iron and aluminum this method will not give accurate results because the phosphates of these metals are insoluble in acetic acid. In such cases, filter the turbid acetic acid solution and determine the phosphoric acid in the filtrate by the above titration. Ignite the precipitate consisting of iron and aluminum phosphates, weigh, and, if it amounts to less than 0 01 g, assume half its weight to be P_2O_5; otherwise determine the phosphoric acid in the precipitate by the molybdate method.

15. Determination of Nickel by Potassium Cyanide[1]

This method, which permits the volumetric estimation of nickel with speed and accuracy even in the presence of iron, manganese, chromium, zinc, vanadium, molybdenum, and tungsten, depends upon the fact that nickel ions react with potassium cyanide in slightly ammoniacal solution, to form a complex anion $[Ni(CN)_4]^{--}$:

$$Ni(NH_3)_6Cl_2 + 4KCN = K_2[Ni(CN)_4] + 6NH_3 + 2KCl$$

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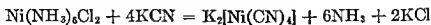
[1] Cf. Campbell and Andrews, *J. Am. Chem. Soc.*, **17**, 126 (1895); Moore, *Chem. News*, **72**, 92 (1895); Goutal, *Z. angew. Chem.*, **1898**, 177; Brearley and Jarvis, *Chem. News*, **78**, 177 and 190 (1898); Johnson, *J. Am. Chem. Soc.*, **29**, 1201 (1907); Campbell and Arthur, *ibid.*, **30**, 1116 (1908); and Grossmann, *Chem.-Ztg.*, **32**, 1223 (1908).

If the solution of the nickel salt contains a precipitate of silver iodide, produced by adding a known amount of silver nitrate and a few drops of potassium iodide solution, the turbidity will not disappear until all the nickel has entered into reaction with the potassium cyanide.

$$AgI + 2CN^- = K[Ag(CN)_2] + I^-$$
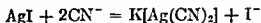
The titration is finished by adding just enough more silver nitrate to cause the precipitate of silver iodide to reappear.

$$I^- + Ag^+ = AgI$$

Requirements. 1. A *nickel solution* of known content. Dissolve 10 g of pure nickel in 125 ml of 6 N nitric acid, boil off the nitrous fumes, and dilute with water to 1 l at 20°.

2. A *silver nitrate solution*. Dissolve 5 g of silver nitrate in water and dilute to 1 l.

3. A *potassium cyanide solution*. Dissolve 15 g of pure potassium cyanide and dilute to 1 l.

4. A *potassium iodide solution*. Dissolve 10 g of potassium iodide in 100 ml of water.

Standardization of the Potassium Cyanide Solution. To 10 ml of the nickel solution, accurately measured with a pipet, add ammonium hydroxide in slight excess, dilute to 100 ml, and add 6 drops of potassium iodide solution and about 1 ml of silver solution from a buret, noting the reading of the buret before adding the silver solution. From another buret, slowly run in potassium cyanide solution, with constant stirring, until the silver iodide precipitate dissolves. Then very carefully add silver nitrate solution until a permanent turbidity is formed and dissolve this by the careful addition of more potassium cyanide solution. Continue in this way until 2 drops of the potassium cyanide solution suffice to dissolve the last silver iodide turbidity produced by adding the silver nitrate solution. Since the potassium cyanide solution decomposes slowly, this titration must be made every day that the solution is used.

Next determine the relative strengths of the silver solution and of the potassium cyanide solution. From a buret, measure out 30 ml of the potassium cyanide solution, neutralize with ammonia, dilute, add potassium iodide, and titrate in exactly the same way as just outlined.

From this last titration in which a ml of silver nitrate was found equal to b ml of potassium cyanide, 1 ml of $AgNO_3$ solution $= b/a$ ml of KCN solution. If T ml of potassium cyanide and t ml of silver nitrate were used in the titration of 10 ml of nickel solution (= 0.1 g Ni), then

$$1 \text{ ml of KCN solution} = \frac{0.1}{T - (b/a)t} \text{ grams Ni}$$

16. Determination of Nickel in Solutions of Nickel Salts

Procedure. To 100 ml of solution containing approximately 0.1 g of nickel, add ammonium hydroxide[1] and continue exactly as in the above standardization with pure nickel solution.

F. Sutton[2] states that, instead of working with two solutions, equally reliable results can he obtained hy using a potassium cyanide solution to which a little silver nitrate has been added. Thus, to the above solution of potassium cyanide there may he added about 0.50 g of silver nitrate which is first dissolved in water by itself. If this solution is used for titrating a niekel solution to which potassium iodide solution has been added, a precipitate of silver iodide is formed at once which increases at first on adding the potassium cyanide-silver nitrate solution until all the nickel is converted into potassium nickeloeyanide, but the precipitate eventually disappears upon the further addition of the solution.

Remarks. Instead of titrating the potassium cyanide against a known niekel solution, the standardization may be accomplished with 0.1 N silver nitrate solution. In this case it is best to take as end point the formation of a slight turbidity on adding silver nitrate, rather than the dissolving of the precipitate with potassium cyanide. One milliliter of 0.1 N silver nitrate solution = 0.01302 g of KCN = 0.002934 g of Ni.

The method can he carried out in the presence of most of the other elements of the ammonium sulfide group. If a clear solution is not obtained on adding ammonium hydroxide, the addition of ammonium chloride sometimes helps. If copper is present in amounts not exceeding 0.4 per cent, the copper will replace almost exactly three-quarters of its weight of nickel. If chromium is present, the dark color due to the presence of chromic salts may be obviated by adding to the original sulfuric acid solution a 2 per cent solution of potassium permanganate until a slight permanent precipitate of manganese dioxide is obtained, whereby the chromium is oxidized to chromic acid. Filter the solution, concentrate in a 400-ml beaker to about 60 ml, then treat with sodium pyrophosphate, as described below. The method is not applicable in the presence of considerable cobalt, which is betrayed by the dark color assumed by the solution upon the addition of potassium cyanide, but when the amount of the latter does not exceed one-tenth the amount of nickel present, the titration can be carried out successfully and the results represent the amount of nickel and cobalt present.

Zinc causes trouble unless alkali pyrophosphate is added. The titration can be carried out in the presence of aluminum, iron, and manganese if citric or tartaric acid or sodium pyrophosphate is added.

The temperature of the solution should not be much above 20°, for in hot solutions the results are not concordant. The quantity of ammonia present should not be too great, because there is a tendency for ammonia to impede the reaction if more

[1] If the addition of ammonia does not give a clear solution, a few cubic centimeters of ammonium chloride solution should be added.
[2] Volumetric Analysis, 8th edition, p. 252.

than a slight excess is present. **Potassium cyanide** containing sulfide cannot be used; the reagent should be the purest obtainable. The results are accurate. The method has been modified so that it can be used to advantage for the determination of nickel in nickel steel.

The following procedure is not applicable in the presence of copper or cobalt, both of which react like nickel with KCN, or in the presence of tungsten, which gives a turbidity of hydrated WO_3 that interferes with the end point.

17. Determination of Nickel in Nickel Steel

Dissolve 1 g of steel in a casserole with 20 ml of 6 N nitric acid, adding a little hydrochloric acid if necessary. (If much chromium is present use 20 ml of 9 N H_2SO_4 and, later, 5 ml of concentrated nitric acid to dissolve carbides.) After the steel has dissolved, add 10 ml of 15 per cent $(NH_4)_2S_2O_8$ solution and boil 5 minutes. Then filter if necessary. Cool, and, to prevent precipitation of $Fe(OH)_3$ on neutralization, add 10 ml of a solution made by dissolving 20 g of citric acid, 27 g $(NH_4)_2SO_4$, and 20 ml of concentrated NH_4OH in 80 ml of water. Cool to room temperature, and add 6 N ammonia until the solution assumes a greenish tint and is basic to litmus. Cool the clear solution to room temperature and dilute to 200 ml with cold water; carefully measure out from a buret about 0.5 ml of the standard silver nitrate solution and add 2 ml of the potassium iodide. Titrate with potassium cyanide until the precipitate of silver iodide has disappeared, and finish by adding just enough more of the silver nitrate to cause the formation of a slight turbidity again.

the solution; if a precipitate is formed which will not dissolve upon stirring, dissolve it in HNO_3. Cool well, add 50 ml of the above-mentioned ammonium citrate mixture, and proceed as described above.

If copper is present, dissolve the sample in 35 ml of 6 N H_2SO_4 and precipitate the unoxidized solution by boiling with about 1 g of 18-gauge pure aluminum wire. Filter, add to the filtrate 5 ml of concentrated HNO_3, boil off nitrous fumes, and then neutralize with ammonia and add citric acid mixture. If more than 0.2 per cent of nickel is present and the copper content is high, it is better to use the dimethyl glyoxime method.

18. Determination of Copper by the Potassium Cyanide Method[1]

Principle. If an ammoniacal solution of a cupric salt is treated with potassium cyanide, the intense blue color gradually disappears. The reaction is essentially as follows:

$$2Cu(NH_3)_4^{++} + 7CN^- + H_2O = Cu_2(CN)_6^{---} + CNO^- + 2NH_4^+ + 6NH_3$$
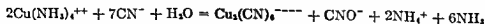
[1] Cf Steinbeck, *Z. anal. Chem.*, **8**, 8 (1869); Dulin, *J. Am. Chem. Soc.*, **17**, 346; A. H. Low, *Technical Methods of Ore Analysis.*

The temperature of the solution, the ammonia concentration, and the quantity of ammonium salts present affect the reaction so that a given quantity of copper does not always react with the same quantity of potassium cyanide. The potassium cyanide solution, therefore, must be standardized under exactly the same conditions as under which the analysis is carried out.

Standardization of the Potassium Cyanide Solution. Dissolve 20 g of pure potassium cyanide in a liter of water. Weigh out 0.2 g of pure copper wire, or foil, into a 200-ml Erlenmeyer flask, and dissolve in 10 ml of 6 N nitric acid. After the copper has dissolved add 25 ml of water and 5 ml of bromine water. Boil to expel the excess of bromine. Then add 50 ml of water and 10 ml of concentrated ammonium hydroxide, cool to room temperature by placing the flask in cold water, and add the potassium cyanide solution slowly from a buret, while constantly rotating the contents of the flask. When the solution has become a pale blue, dilute to about 150 ml and continue adding the potassium cyanide until the solution is just decolorized. The weighed amount of copper divided by the number of milliliters of potassium cyanide required gives the titer of the solution.

Low's Method for Analyzing Copper Ores. Weigh out 0.5 g of a rich ore, or from 2 to 4 times as much of a low-grade ore, into a 200-ml Erlenmeyer flask and treat with 6-10 ml of concentrated nitric acid. Boil until nearly all the red fumes are expelled. If necessary, also add 5 ml of concentrated hydrochloric acid to decompose the ore and continue boiling for a short time. After cooling somewhat, add 14 ml of 18 N sulfuric acid and evaporate until dense fumes of sulfuric acid are evolved. Then, after allowing to cool again, add 25 ml of cold water and a drop of concentrated hydrochloric acid to precipitate any silver as chloride. Boil to dissolve the copper and ferric sulfates, and filter off the precipitated lead sulfate and silicious residue. Wash the residue with hot water and receive the filtrate in a 150-ml beaker, taking care not to let the filtrate exceed 75 ml.

Place a piece of sheet aluminum, about 14 cm long and 2.5 cm wide and bent into a triangle, in the beaker. Cover with a watch glass, and boil the contents of the beaker for about 10 minutes, whereby nearly all the copper is deposited as spongy metal. Now remove the flame and wash down the sides of the beaker with cold water. To precipitate the last traces of copper and to prevent the oxidation of the fine deposit, add 15 ml of strong hydrogen sulfide water and decant the liquid through a 9-cm filter. Wash off the copper from the aluminum by means of weak hydrogen sulfide water into the flask in which the ore was dissolved and decant the liquid through the filter. Set aside the beaker containing the aluminum foil and some copper. The

operation of filtering should take place without interruption and the filter kept well filled with liquid to prevent the oxidation of any precipitate upon it, which would cause it to dissolve and give a turbid filtrate. After washing the deposit 4 times, using in each case 20 ml of weak hydrogen sulfide water, allow the liquid to drain from the funnel, and then replace the beaker containing the filtrate with the flask containing the deposited copper. Cover the aluminum foil, to which some copper usually adheres, with 10 ml of 6 N nitric acid, heat nearly to boiling, and pour the hot acid through the filter. Replace the flask with the beaker containing the foil, and heat the contents of the flask until all the copper is dissolved and the greater part of the red fumes expelled. Again place the flask under the funnel, cover the aluminum foil in the beaker with 5 ml of strong bromine water, and pour this through the filter. Then wash the aluminum foil and the filter with hot water. Boil the solution to expel the excess of bromine, cool to room temperature, treat with 10 ml of strong ammonia, and titrate with potassium cyanide exactly as in the standardization.

19. Determination of Lead by the Molybdate Method[1]

Principle. The lead is precipitated as molybdate from an acid solution, and the termination of the reaction is recognized by testing a drop of the solution with a drop of tannin solution, which gives a yellow coloration when an excess of ammonium molybdate is present.

Requirements. 1. A solution of ammonium molybdate prepared by dissolving about 4.25 g of ammonium molybdate in water, and diluting to 1 l.

2. A freshly prepared tannin solution containing 0.1 g of tannin in 20 ml of water.

Standardization of the Ammonium Molybdate Solution. Weigh out 0.2 g of pure lead foil into a 200-ml Erlenmeyer flask, dissolve in a mixture of 2 ml concentrated nitric acid and 4 ml of water, and evaporate the solution nearly, if not quite, to dryness. Take up the residue in 30 ml of water, add 5 ml of concentrated sulfuric acid, shake, and allow the lead sulfate to settle completely. Filter and wash the precipitate with 3.5 N sulfuric acid. Drop the filter, together with precipitate, into an Erlenmeyer flask, add 10 ml of concentrated hydrochloric acid, and boil the liquid until the filter is completely disintegrated. Then, after adding 15 ml more of concentrated hydrochloric acid and 25 ml of cold water, carefully add 25 ml of concentrated ammonia, whereby the greater part of the acid is neutralized. Drop a piece of blue litmus paper into the solution, add ammonia to slightly alkaline reaction, and then glacial acetic acid until the litmus paper turns red. Dilute

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[1] Alexander, *Chem.-Ztg.*, 16, 181 (1892); Low, *Technical Methods of Ore Analysis*.

to about 200 ml with hot water and transfer about two-thirds of the solution to a beaker. Add the ammonium molyhdate solution to the beaker from a huret until a drop of the solution, brought in contact with a drop of the tannin indicator upon a white porcelain tile, gives a brown or yellow color. Pour in some more of the lead solution to the beaker and repeat the operation until only a few milliliters of the lead solution remain in the flask. Finally add the rest of the solution, and finish the titration hy adding the molybdate solution 2 drops at a time. If t ml of molybdate is used in titrating a g of lead the titer of the solution is

$$1 \text{ ml ammonium molyhdate} = \frac{a}{t} \text{ g lead}$$

Procedure.[1] Dissolve the ore in hydrochloric acid or hydrochloric and nitric acids, and filter the solution while hot without diluting any more than to prevent the acid attacking the ore. Wash the residue rapidly with a hot solution of ammonium chloride until the washings show no blackening when tested with ammonia and a drop of ammonium sulfide. Make the filtrate just alkaline with ammonia and add a slight excess of ammonium sulfide. Heat to boiling, filter off the precipitated sulfides, and wash with hot water. (The alkaline earths may be determined in the filtrate if desired.) Dissolve the sulfides in hot, dilute nitric acid and catch the resulting solution in the same beaker in which the sulfides were precipitated. Add 7 ml of concentrated sulfuric acid, and evaporate the liquid until dense vapors of sulfuric acid are evolved. After allowing to cool, add 25 ml of water and boil the liquid to dissolve the anhydrous ferric sulfate. Add 10 ml of alcohol, cool to room temperature, and filter off the precipitated lead sulfate. Wash free from acid, dissolve in a slight excess of ammonium acetate solution,[2] and dilute with water. After heating to boiling, titrate the hot solution with ammonium molyhdate.

The above procedure serves when alkaline earths are present; hut when these are known to he absent, the original solution of the ore can be at once evaporated with sulfuric acid, the resulting lead sulfate dissolved in ammonium acetate solution and titrated without any purification.

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[1] This method was obtained through the courtesy of Mr. Franklin G. Hills of the American Smelting and Refining Co.

[2] If too much ammonium acetate solution is used, a transitory end point is obtained in the subsequent titration. It is necessary to use a hot solution, which does not contain too much of the salt. See p. 59.

20. Determination of Zinc by Potassium Ferrocyanide[1]

The potassium ferrocyanide method for titrating zinc is very accurate but it requires some experience before an operator becomes skilled in its use. The end point of the reaction corresponds to the formation of $K_2Zn_3[Fe(CN)_6]_2$.

$$3ZnCl_2 + 2K_4Fe(CN)_6 = 6KCl + K_2Zn_3[Fe(CN)_6]_2$$
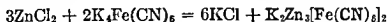
After this point is reached, a slight excess of ferrocyanide will give a brown coloration when tested with dilute uranyl solution or ammonium molybdate on a spot plate. If the solution contains a very small quantity of iron, a little prussian blue is formed and the color changes from pale blue to pea green at the end point as a result of the presence of yellow ferrocyanide.

Potassium Ferrocyanide Solution. Dissolve 32.31 g of pure $K_4Fe(CN)_6\cdot3H_2O$ in water and dilute 1 l; 1 ml of this solution should react with 7.5 mg of zinc.

Standardization. Weigh out into 400-ml beakers several 0.3-g portions of pure zinc, weighing to 4 decimal places. Cover with water and dissolve in 20 ml of 6 N hydrochloric acid. When all the zinc has dissolved, neutralize with strong ammonia, make slightly acid with hydrochloric acid, and add 0 ml of 6 N acid in excess. Add 2 drops of ferrous sulfate solution containing 2.5 g $FeSO_4\cdot7H_2O$ per liter. This corresponds to about 0.03 mg of iron. Dilute with water to 200 ml, heat to boiling, and titrate as follows: Reserve one-quarter of the solution in a small beaker, to avoid the necessity of titrating to the right end point at once. To the hot solution add the ferrocyanide with vigorous stirring. The solution assumes a blue color, which should be quite pale and is due to the reaction of ferrocyanide with a very small quantity of ferric iron formed from the ferrous solution added. When an excess of yellow ferrocyanide is present, the blue color changes to a pale green. Add a little more of the ferrocyanide and pour in all but about 5 ml of the reserved zinc solution. Again add ferrocyanide till the end point is reached and about 0.5 ml more. Add the last of the reserved solution, wash out the beaker with hot water, and titrate with ferrocyanide dropwise until the blue color fades sharply to a pea green. This is the end point.

Repeat the standardization until an agreement within 2 parts in 1000 is obtained.

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[1] The directions here given are based upon the procedure followed in the laboratories of the New Jersey Zinc Company at Palmerton, Pa.

Analysis of the Ore. Weigh out into a small beaker enough of the powdered ore to give approximately 0.6 g of zinc. Moisten with water and add 10 ml of concentrated hydrochloric acid. If sulfides are present it may be necessary to add 10 ml of concentrated nitric acid at this point. Digest on the hot plate at a temperature below the boiling point for 1 hour. Remove from the plate and wash down the sides of the beaker and the cover glass. Add 10 ml of 18 N sulfuric acid and evaporate to fumes. With very silicious material it is well to break up the silica with a glass rod before adding the sulfuric acid. Cool and dilute to 50 ml with water.

If there is any indication of undecomposed mineral in the residue filter and wash the residue with hot water. Digest the residue with hot ammonium acetate solution to remove lead sulfate and treat the residue with sulfuric and hydrofluoric acids (cf. silicate analysis). Then, after the removal of the excess acid, fuse with potassium pyrosulfate, dissolve the melt in dilute sulfuric acid, and add the solution to that previously obtained.

The next step is to reduce the ferric salt and precipitate copper, bismuth, etc., by treatment with 1 g of 20-mesh aluminum powder at a volume of about 50 ml. If it was not necessary to test the residue for zinc, the treatment should precede the filtering of the lead sulfate and silica precipitate. Add 10 drops of saturated sodium thiosulfate solution, cover the beaker with a watch glass, and heat 20 minutes. This serves to reduce the iron and precipitate all the copper-group metals except about 0.05 per cent of cadmium, which does no harm. Transfer the solution to a 200-ml measuring flask. Make up to the mark, mix, and filter through a dry paper. Reject the first 10 ml of runnings and take 100 ml for the titration. Transfer the solution to a tall, 400-ml beaker, and neutralize with sodium hydroxide solution till a jelly is formed (of Al(OH)₃) and the acidity corresponds to about 2 drops of 20 per cent sulfuric acid. Use methyl orange as indicator. Add 3 ml of 5 per cent sulfuric acid, dilute to 200 ml, and introduce a stream of hydrogen sulfide into the cold solution for 40 minutes, at the rate of at least 8 bubbles per second. Allow the precipitate to settle for 15 minutes, filter, and wash with cold water.

Wash back the zinc sulfide precipitate into the beaker and rinse out the hydrogen sulfide tubing with 10 ml of concentrated hydrochloric in hot water. Run the acid through the filter and wash with hot water. Heat the acid until all the zinc sulfide has dissolved and all the hydrogen sulfide is expelled. Dilute with cold water to 150 ml, add concentrated ammonia until slightly alkaline, neutralize with hydrochloric acid, and continue as in the standardization of the ferrocyanide solution.

21. Determination of Arsenic in Ores. Modified Method of Low-Pearce-Bennett

Of the finely powdered ore, take 0.5 g if the arsenic content is not above 10 per cent. If the ore is richer, take only enough to furnish 0.05–0.10 g of arsenic. Mix the ore with 2 g of anhydrous sodium carbonate and 1.5 g of potassium nitrate in a 30-ml porcelain crucible, and sprinkle about 1 g of the fusion mixture on top. Cover the crucible and heat very slowly over a small flame, gradually raising the temperature until finally the full heat of a good burner is used for 10 minutes. Cool and extract with 200 ml of hot water. Filter and wash with hot water until all the soluble alkali salts are removed as shown by the litmus test for sodium carbonate. In this way all the arsenic is obtained as alkali arsenate.

Make the solution distinctly acid with acetic acid and boil 10 minutes to remove carbonate and nitrite. Cool and add sodium hydroxide until the solution is basic to phenolphthalein. Discharge the color with a few drops of acetic acid and add 20 ml of 0.1 N silver nitrate solution. After the reddish brown precipitate of silver arsenate has coagulated sufficiently, filter and wash with cold water till the washings are free from silver. Dissolve the silver arsenate by pouring small portions of hot 3 N nitric acid through the filter, using about 10 ml of acid in all. Dilute and titrate the silver by the Volhard method, p. 648. One milliliter of 0.1 N KCNS solution = 0.002499 g of As.

Remark. This method gives excellent results in the commercial analysis of arsenide ores, but chromium and phosphorus interfere as silver chromate and phosphate, etc., behave like the arsenate.

PART III. GAS ANALYSIS

CHAPTER XVIII

GENERAL CONSIDERATIONS

The chemical analysis of gas mixtures is accomplished usually by measuring and rarely by weighing the individual constituents, so that it is customary to express the results in percentage by volume. Strictly speaking, the original gas has each individual constituent throughout the entire volume, and the sum of the pressures exerted by the individual constituents is the pressure of the entire gas. When we say that air contains about 20 per cent oxygen and 80 per cent nitrogen by volume we mean that if we were to take 20 ml of oxygen and 80 ml of nitrogen (both measured at atmospheric pressure) we would have the equivalent of 100 ml of air although in the mixture each gas is uniformly distributed and has a volume of 100 ml; the sum of the pressures exerted by each gas at that volume is equal to the atmospheric pressure. Inasmuch as the volume of a gas is influenced to a marked degree by the temperature and pressure, it is necessary to reduce each measurement to standard conditions of temperature and pressure, and further to take care that these remain constant during the whole of the analysis. A volume of gas V measured over water at $t°C$ and B mm barometric pressure[1] is reduced to the volume which it would assume at 0°C and 760 mm pressure in a dry condition by means of the formula

$$V_0 = \frac{V(B - w)}{760 (1 + \alpha t)}$$

In this formula, V_0 represents the reduced volume,[2] V the volume

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[1] Here is understood the barometer reading reduced to 0°C. The reduction is accomplished by means of the formula: $B_0 = \dfrac{1 + \beta t}{1 + \alpha t} \cdot B$, in which B_0 represents the reduced reading, B the actual reading at t_0, α the expansion coefficient of mercury (= 0 000181), β the linear coefficient of expansion of glass (= 0.0000085). For most purposes, however, the reduction to 0°C can be made with sufficient accuracy by making the following deductions from the actual readings:

5–12°	1 mm	21–28°	3 mm
13–20°	2 mm	29–35°	4 mm

[2] Or volume under *standard conditions*.

of the gas at $t°C$ and B mm pressure, w the tension of aqueous vapor, and α the expansion coefficient of the gas (= 0.003665).

As, however, $\alpha = \dfrac{1}{273}$, the above formula may be written as follows:

$$V_0 = \frac{V(B - w)\,273}{760\,(273 + t)}$$

Instead of reducing the observed volume to the standard conditions by computation, it can be effected mechanically by compression (see p. 330).

The Collection and Confinement of Gas Samples

Since all gases diffuse rapidly into one another even when separated by porous solid bodies or liquids, it is evident that the collection of the sample and its preservation offer certain difficulties. If a gas is confined in a bell jar over water and thus kept out of contact with the air, it will be found that different results will be obtained in the analysis of the gas from day to day. The air gradually penetrates through the water into the bell jar, and in the same way the gas within the jar gradually diffuses into the atmosphere. This process will continue until finally the composition of the gas both within and without the jar is the same. The rapidity of the diffusion depends upon the extent to which the gases are absorbed by the liquid which separates them. Those liquids which absorb the gases readily, allow them to pass through it rapidly, and consequently cannot be used for keeping the gases apart. Of all liquids, mercury is best suited for the purpose, because it absorbs only minimum amounts of the different gases.

Gases which combine chemically with mercury, such as chlorine, bromine vapors, and hydrogen sulfide, cannot, of course, be collected over mercury; it is best to collect them in dry glass tubes and to seal the tubes by fusing together the open ends if the gas cannot be analyzed immediately. Through glass there is no diffusion, so that gases may be kept unchanged in sealed tubes for years.

If the gas is to be analyzed within a few days after the time of collection, it can be kept in pipet-shaped tubes. The ends are closed by thick pieces of rubber tubing into each of which is inserted a piece of glass stirring rod with rounded ends; where the rubber tubing comes in contact with the glass it should be fastened tightly with wires. It is not permissible to keep gases in such tubes for a considerable length of time, for rubber, particularly when it has become hard, permits the diffusion of gases to some extent.

For less accurate analyses, the gases can be collected over water which has been previously saturated with the gas to be analyzed, and the analysis must be made immediately afterwards.

From what has been said, it is evident that care must be taken in collecting and keeping the gas to be analyzed. We will now consider briefly a few practical examples.

(a) Collection of Gases in Accessible Places

1. Draw out the neck of a 200-ml flask somewhat and insert a glass tube (Fig. 95). Draw about 800 ml of the gas to be analyzed through the flask by means of suction. Then close the neck of the flask by means of a rubber cap and fuse the glass together.
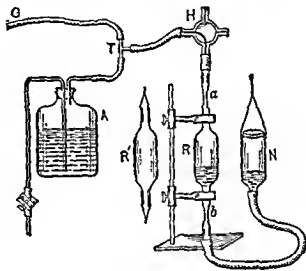
Fig. 95.   Fig. 96.

(b) Collection of Gases from Inaccessible Places

Connect the rubber tubing G, Fig. 96, on one side with the aspirator A of about 30-l capacity and on the other with the source of the gas, and allow water to flow quickly from the aspirator. After 5 or 6 l has run out, the air is usually completely expelled from the rubber tubing and replaced by the gas to be analyzed, so that it is now ready for collecting the same. For this purpose, turn the stopcock H 90° to the right, so that the vessel R, which is to receive the gas, is in communication with the outer air, and expel the air from it by raising the mercury reservoir N. Then turn back the stopcock to the position shown in the figure and fill R with the gas by lowering N. As the tubing between the T tube and the stopcock contained impure gas,

again fill R with mercury and expel the gas into the air. After the process has been repeated 3 times, fill the receiver for the last time with the gas, close H, lower N so that the pressure in the tube is less than that of the atmosphere, and fuse together the ends of R first at a then at b. During this sealing of the tube, it should be removed from the ring-stand so that the tube can be revolved a little while being heated in the flame.

In sealing the tube, draw out the ends into a capillary as shown in R', Fig. 96.

If it is necessary to obtain the gas from places at a very high temperature, e.g., from blast furnaces, producers, etc., glass tubes would melt, and if ordinary iron tubes were not melted they would decompose the gas. In this case it is best to use the water-jacketed iron tube devised by St. Claire Deville and shown in Fig. 97. Cause cold water to run into the outer condenser at a and to run out at b, and collect the gas, as described above, through the tube c. It is important that the water should run through the tube fast enough to keep the inner tube cold; otherwise the gas will be decomposed. By this means there is no difficulty in collecting gas samples from different heights of the glowing layers of coal in blast furnaces or producers, or from smoke stacks.
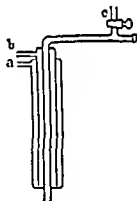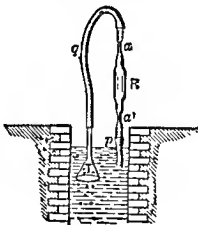
FIG. 97.   FIG. 98.

Collection of Gases Arising from Mineral Springs

Connect the receiver R with the funnel T by means of the rubber tubing q (Fig. 98). Fill all these parts of the apparatus with spring water and allow the gas to ascend through the funnel as shown in the illustration. In order that the gas may pass from the funnel into the receiver, raise R, so that only the tubing p remains in the water, and lower the funnel as far as possible, causing pressure enough to drive

tbe gas over. Then close tbe tubing just above a by means of a screw-
cock, place a beaker filled with spring water under p, remove the
apparatus from the spring, fuse together both ends of R with the blow-
pipe. If the gas is to be analyzed within 2 or 3 days, tbe receiver may
be closed by pieces of short rubber tubing each containing a short piece
of glass rod with rounded ends. All such connections must be fas-
tened by means of wires where the glass comes in contact with tbe rubber.
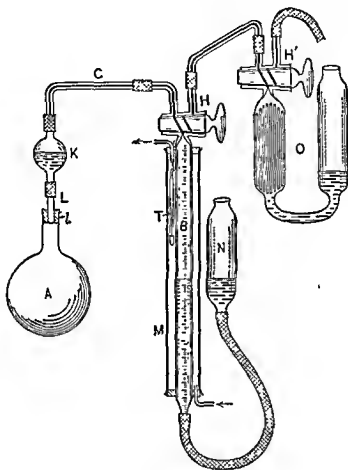
FIG. 99.

Collection of Gases Absorbed in Spring Water

Of tbe many different methods which have been proposed for the
analysis of tbe absorbed gases in spring water, the following is prob-
ably tbe most satisfactory.

Fill tbe flask A, Fig. 99, with spring water up to its upper edge and
immediately insert in the neck of the flask and press down tbe rubber
stopper containing tbe tube L, which is fused together at tbe bottom
but bas an opening on the side at l. Raise tbe tube L so that tbe

opening l is within the stopper, thus making an air-tight connection. Now connect the bulb K with L, which is half full of distilled water and is connected with the capillary tubing C, although the latter is not yet connected with the measuring tube B, as shown in the illustration. Raise the leveling tube N until mercury begins to flow out of the right-angled capillary tube, then close the stopcock H. After this boil the water in the bulb K (which is held in an inclined position) for 3 minutes, meanwhile warming the capillary tubing connected with the measuring tube. Unless this last precaution is taken, the capillary tubing is likely to break, particularly in winter. After the water in K has boiled vigorously for 3 minutes, remove the flame, quickly connect C with the measuring tube B, and securely fasten the rubber connection with wire. By boiling the water in K, a complete vacuum is produced in the bulb, so that the gas can be collected at once from the spring water. For this purpose press down the tube L through the rubber stopper until the opening l comes just below its lower edge, lower the leveling tube N, and open the stopcock H. At once there is a lively evolution of gas from the water in A, and this is subsequently maintained by warming the water. As soon as the eudiometer is full, close the stopcock and read the volume of the gas after bringing the mercury to the same level in N that it is in B. At the same time note the temperature of the water into the condenser M and read the barometer. Drive over the gas into the Orsat tube, O, containing potassium hydroxide solution (1 : 2), and allow it to remain there for the time being. Meanwhile continue boiling the water in A, and measuring the gas in B, etc., until finally no more gas can evolve from the spring water. Drive over all the gas into the Orsat tube, after its volume has been noted; by means of the caustic potash, the carbonic acid is quantitatively absorbed. Again drive the unabsorbed gas over into B and read its volume. By correctly regulating the velocity of the current of water flowing through the condenser, it is easily possible to maintain a constant temperature throughout the whole of the experiment. The residual gas remaining after the absorption of the carbon dioxide consists usually of nitrogen, oxygen, and in some cases methane. Transfer it to the apparatus of Hempel, and analyze according to methods which will be described further on.

According to this method, the determination of nitrogen, oxygen, and methane gives exact results, but the apparent amount of carbon dioxide is sometimes too much and sometimes too little. If the water contains large amounts of bicarbonate in solution, the carbonic acid found will represent more than was originally present in the free state, for such substances are partly decomposed by boiling their aqueous

solution.   On the other hand, if only a little hicarbonate is present, the result will be too low, for it is not possible to remove all the free carbonic acid from a solution by boiling it in a vacuum.

Consequently, in all cases the free carhonic acid must he determined hy computation.   For this purpose determine the total carbonic acid in a fresh sample of the water, according to p. 336, and then, if the composition of the solid constituents present is known, the volume of the free carhonic acid can he calculated.

Example.   One thousand grams of Tarasper-Lucius water contains 7.877 g of total carbonic acid.   Of this amount, a part is present in the water as bicarbonate, and the remainder is *free* carbonic acid.   If from the total amount of carbonic acid the *combined* acid is deducted, the difference represents the amount of free carbonic acid present.

Calculation of the Carbonic Acid Present as Bicarbonate

This is ohtained by multiplying the difference between the cations and anions (expressed in gram equivalents) hy the molecular weight of HCO_3, because the sum of the cations in every salt solution is equal to that of the anions present when both are expressed in gram equivalents.

The gram equivalents are ohtained by dividing the weight in grams of each clement (or radical) hy the respective atomic (or molecular) weight and multiplying by the valence.

By hoiling 828.3 g of the water, 1868.9 ml of CO_2 was ohtained at 8.4° and 651 mm pressure, containing only traces of nitrogen.   This corresponds to 1851 ml per liter, at 0° and 760 mm pressure, which is more than the calculated amount, because by hoiling some of the hicarbonate was decomposed.

CALCULATION OF THE MILLIEQUIVALENTS

1000 g of Lucius water contains:

Cations	Wt. in mg	Milliequivalents
Potassium (K+)	166	4.24
Sodium (Na+)	3906	169.4
Lithium (Li+)	9	1.30
Ammonium (NH₄+)	13	0.72
Calcium (Ca++)	627	31.34
Strontium (Sr++)	9	0.20
Magnesium (Mg++)	190	15.60
Iron (Fe++)	6	0.20
Manganese (Mn+++)	0.2	0.009
Aluminum (Al+++)	0.6	0.072

Sum of cations 223.08 milliequivalents

	Anions	*Wt. in mg*	*Milliequivalents*
Chloride (Cl⁻)	....	2400	67.7
Bromide (Br⁻)	....	29.	0.36
Iodide (I⁻)	....	0.9	0.007
Sulfate (SO₄⁻⁻)	....	1727	36.02
Hydrophosphate (HPO₄⁻⁻)	....	0.08	0.018
Hydrocarbonate (HCO₃)	....	?	

<div align="right">104.1 milliequivalents</div>

Sum of cations   223 1
Sum of anions   104.1

Bicarbonate ions 119 0 = 119 × 0.06101 = 7.262 g HCO_3 = 5.240 g CO_2

CALCULATION OF FREE CARBONIC ACID

Total CO_2 = 7.877 g; combined CO_2 = 5.240 g; free CO_2 = 2.637 g = 1334 ml at 0° and 760 mm pressure.

If the amount of bicarbonate present is very small, the total amount of carbonic acid obtained by boiling the water is always too small. Thus with the thermal water of Baden, by boiling there was obtained:

Nitrogen	14.43 ml per liter
Carbon dioxide	112.12 ml per liter
	126.55 ml per liter

and from the analysis, the free carbonic acid was computed to be 180.52 ml. The absorbed gas in the thermal water of Baden is, therefore,

Nitrogen	14.43 ml per liter
Carbon dioxide	180.52 ml per liter
	194.95 ml per liter

Remark. With the above method of collecting the gas, it is difficult to prevent some water getting into the measuring tube B, by means of which a small amount of the gas will be reabsorbed This difficulty is avoided, however, if the flask shown in Fig 100 is used to contain the water.

This flask is provided with a short tube blown into its neck near the top and connected by means of thick-walled rubber tubing with the mercury reservoir R. In order to determine the contents of the flask, make a scratch on the small tube about 4 cm from the neck of the flask, drive over the mercury just to this mark, and tightly close the rubber tubing by means of a screwcock. Then empty the reservoir of mercury, and weigh the flask together with the stopper, glass tube L, rubber tubing, and what mercury remains above Q Next fill the flask with water, press down the stopper to the mark in the neck of the flask, and raise the tube L until the lower opening l comes within the stopper. After drying the tube L with blotting paper, weigh the flask and its contents. Etch its capacity upon the bulb of the flask.

For the determination of the gases absorbed in a liquid, fill the flask A in the same way as in the determination of its capacity, connect the bulb tube K, half filled with

distilled water, with L, and connect L with a capillary tube as shown in Fig 99. Remove the air from K and the capillary tubing by boiling the water in K, as described on p. 675, and then connect the capillary with the measuring tube B, Fig. 99. Next connect the heavy rubber tubing with the reservoir as shown in Fig. 100, and place the latter in a beaker of hot water. Introduce the tube L into the neck of the flask
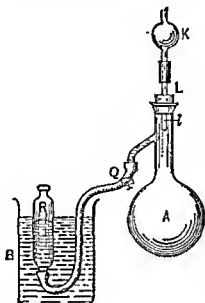
FIG. 100.

until the opening l can just be seen, and expel the gas in the same way as described on p. 675, except that this time the liquid is not allowed to rise so high in K. After three-quarters of an hour the gas will be completely expelled from the liquid. Drive over the last portions of the gas into B by lowering the leveling tube N (Fig. 99), raising the mercury reservoir R (Fig. 100), and carefully opening the screw clamp Q. A warm stream of mercury will then flow into the flask, expelling the gas into the measuring tube. As soon as the liquid in A has been driven over as far as the stopcock, H, immediately close H. Otherwise the procedure is the same as was described on p. 675.

The Transference of Gases in Sealed Tubes to the Apparatus Used for the Analysis

Assume the gas to be contained in R, Fig. 101. Place a piece of thick-walled rubber tubing, containing a piece of heavy tubing r, over one of the short tubes connected with the three-way stopcock H. Turn the stopcock so that the rubber tubing is above it, and fill the tubing with mercury. Then turn H 180° toward the left so that the left and upper tubes communicate with each other. As soon as the mercury begins to run out, close the stopcock. Then introduce one end of R into the rubber tubing containing the mercury so far that its drawn-out point reaches within r, and fasten the rubber tubing securely by wiring,

using annealed iron wire because copper or brass wire would be likely
to become amalgamated with mercury. In a similar way, connect
the other end of R with the rubber tubing filled with mercury of the
leveling tube N, and after this connect the stopcock H with the meas-
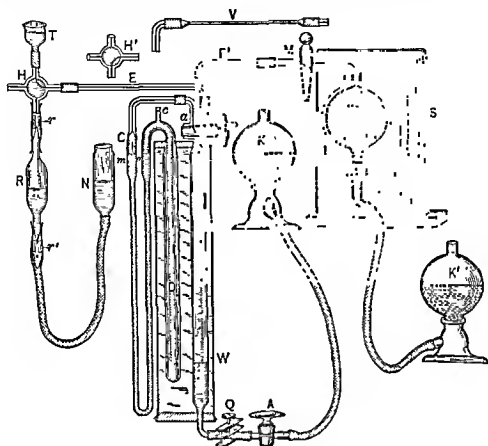
Fig. 101.

uring apparatus W by means of the capillary tubing E. By raising
the leveling bulb K, expel the air from W and the capillary E, and
allow mercury to rise in the funnel T. Turn the stopcock H so that
communication is established between R and W, and open the ends of
R by pressing the capillaries against r and r'. Then, by raising N
and lowering K, drive over the gas into W.

Calibrating Gas Measuring Vessels

When vessels are purchased to be used in measuring gases, the cor-
rectness of the calibrations should always be tested; the testing can
be done with water or with mercury. The calibration with water is
carried out in exactly the same way as was described for vessels to be

used in measuring liquids (cf. pp. 437–446). The calibration by means of mercury will be illustrated by an example. Assume that it is desired to calibrate the apparatus shown in Fig. 102. The vessel must be thoroughly cleaned (cf. p. 437) and then placed in a vertical position as shown in Fig. 102. Connect the lower capillary a by means of thick-walled rubber tubing with a leveling vessel containing mercury,

Fig. 102.

and cause the mercury to rise slowly in the vessel to a little above upper mark. Then close the stopcock, remove the leveling tube together with the rubber tubing, and allow the mercury to flow out slowly until the highest point in the meniscus is exactly tangent to the horizontal plane through $\alpha'\alpha'$. To avoid a parallax error, take the reading with a telescope placed 2 or 3 mm away from the glass. Next allow the entire contents of the vessel, including the space in the stopcock, to run into a tared flask, and weigh to the nearest centigram. After determining the temperature of the mercury, its volume can be found by means of the table (p. 681) prepared by Schlösser.[1]

If the weight of the mercury at 20.3° amounted to 2025.26 g., then its volume corresponds to $\frac{2025.26}{13.5483} = 149.41$. Since, however, mercury forms a convex meniscus and the volume is desired up to the plane $\alpha\alpha'$, it is evident that the volume of mercury weighed did not include the space $\alpha'\alpha–\alpha\alpha'$, and, moreover, since the instrument is to be used in the reversed position, the error is really twice as much, as is evident from the inspection of Fig. 102 I. This is called the *double meniscus correction*. Its value is dependent upon the bore of the tube, as is shown by the table on p. 682.

If the diameter of the vessel in question is 20 mm, then the correction, according to the table, would be 4.016 g, and the true volume will be $\frac{2025.26 + 4.02}{13.5473} = \frac{2029.28}{13.5483} = 149.78$. The volume of this instrument, therefore, is 0.22 cm less than the intended 150 ml. The volume of the narrower parts of the tube can be found in a similar manner.

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[1] Schlösser and Grimm, *Z. Chem. App.-Kunde*, **2**, 201 (1907).

The diameter of the tube is best determined by filling with mercury up to a mark, then allowing it to run out until a lower mark is reached, weighing the escaped mercury, and measuring the distance between the two marks with a millimeter rule. If the weight of the mercury is p, the distance between the marks h, the temperature of the mercury 20.3°, then the

$$\text{diameter} = 2\sqrt{\frac{p}{h \times \pi \times 13.5483}}$$

WEIGHT OF 1 ML OF MERCURY IN AIR AT TEMPERATURES BETWEEN 15° AND 30°

Normal temperature 15°

Temperature of Mercury	Weight	Temperature of Mercury	Weight	Temperature of Mercury	Weight
°C	g	°C	g	°C	g
15	13.5593	20	13.5489	25	13.5385
15.5	13.5583	20.5	13.5479	25.5	13.5374
16	13.5573	21	13.5468	26	13.5364
16.5	13.5562	21.5	13.5458	26.5	13.5353
17	13.5552	22	13.5447	27	13.5343
17.5	13.5541	22.5	13.5437	27.5	13.5332
18	13.5531	23	13.5426	28	13.5322
18.5	13.5520	23.5	13.5416	28.5	13.5312
19	13.5510	24	13.5405	29	13.5301
19.5	13.5499	24.5	13.5395	29.5	13.5291
				30	13.5280

In many cases it is sufficiently accurate to compute the diameter from the circumference of the tube and then subtract twice the thickness of the glass.

If it is desired to determine the total volume of a tube provided with stopcocks at both ends, the apparatus is weighed empty and then filled with mercury. In this case, it is obvious that no meniscus correction is necessary.

For a measuring vessel calibrated with water, when in a reversed position, the meniscus correction is obtained from the table on p. 682. If an instrument calibrated with water is to be used subsequently with mercury, the water meniscus in calibrating the reversed tube occupies a position similar to that of the mercury meniscus when the instrument is in use (see Fig. 103) but the mercury meniscus is not so deep as that of the water. The volume of the gas is therefore found as much too

TABLE OF MENISCUS CORRECTIONS*

Diameter of Tube in mm	Double Meniscus Correction for Hg in mg	Double Meniscus Correction for H₂O in mg = milliliters	Simple Meniscus Correction (H₂O − Hg) in milliliters
3	76	12	3
4	108	20	6
5	174	31	9
6	314	44	10
7	550	61	10
8	790	81	11
9	1038	106	15
10	1288	134	20
11	1540	167	27
12	1796	204	36
13	2058	245	46
14	2326	289	59
15	2596	336	72
16	2872	387	88
17	3152	441	104
18	3436	499	123
19	3726	560	143
20	4016	624	164
21	4314	691	187
22	4614	757	208
23	4920	821	229
24	5230	881	247
25	5544	938	264
26	5864	991	279
27	6185	1042	293
28	6515	1090	308
29	6845	1135	315
30	7182	1179	324

* W. Schlösser. Private Communication

large as there is difference between the simple meniscus corrections for water and mercury. Thus if the volume of a gas-measuring instrument of 10-mm diameter is found by weighing with water to be 10.167, according to the above table, then if the instrument is to be used with mercury, the gas volume will be $10.167 - 0.020 = 10.147$ ml.

Purification of Mercury. Lothar Meyer's Method[1]

The mercury used for gas-analytical operations must be purified. The principal impurities are copper, cadmium, zinc, and sometimes

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[1] *Z. anal. Chem.*, **2**, 241 (1863). C. J. Moore (*Chem.-Ztg.*, **1910**, 735) has used a similar apparatus for purifying large quantities of mercury, but filters through buckskin before allowing it to fall through the acid.

silver and gold. The base metals are removed most readily by allowing the mercury to run in a fine stream through about a meter of 8 per cent nitric acid. This is done in the apparatus shown in Fig. 104. First fill the bottom of the tube B with impure mercury and add the nitric acid. Then pour the mercury through the funnel A, the stem
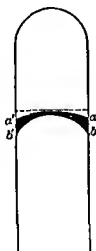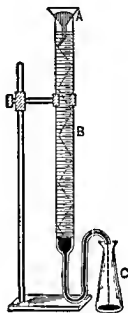
Fig. 103.   Fig. 104.

of which is drawn out to a capillary and bent to an angle of 60°. This causes the mercury to take a zigzag course as it flows slowly through the nitric acid. The dry mercury that first passes over into the flask C is impure and must be poured into the funnel and allowed to flow through the acid. In this way a fairly pure mercury is obtained which can be used as it is for most purposes. If the mercury is to be used for calibrating apparatus, it must be distilled.

For this purpose, Hulett's apparatus, shown in Fig. 105, can be used. Place the mercury in the long-necked flask k and connect with the receiver V. Cover the flask with a mantle of asbestos paper and heat on the sand bath. Through the arm a, connect the receiver with a suction pump and introduce into the flask, through b and the long glass tube that ends in a capillary, a slow current of nitrogen (or carbon dioxide) which has been dried by passing over calcium chloride. Regulate the distillation so that the mercury condenses in the glass arm s, where it leaves the mantle of asbestos paper. About 150–200 ml of mercury can be distilled in an hour with this apparatus. Frequently, especially when the nitrogen used contains a little oxygen, the distilled

mercury is covered with a thin coating of oxide. This may be removed by filtration. To filter the mercury, perforate the point of a paper filter several times with a needle, place the filter in a funnel, and pour the mercury upon the filter. The pure metal runs through the holes in the paper while the impurity remains behind.
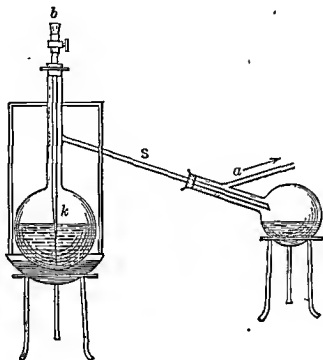
FIG. 105.

For the distillation of large quantities of mercury the apparatus[1] shown in Fig. 106 is suitable. Place the mercury in the container R (an inverted bottle with the bottom cut off). The tubing that rises above R is about 5 mm in diameter and that below is only 2 mm wide. The flask K has a capacity of about 300 ml and is fastened by a clamp to an iron rod attached to the wall of the room. The lower end of the long neck of K reaches nearly to the bottom of R. By suction applied at a produce a partial vacuum in K. This causes mercury to rise in the tube from R into K. Light the ring burner at $B–B'$ upon which the flask K rests. Keep the suction working. The mercury soon boils and the vapor escapes into the tube but is condensed by the cooler liquid and falls in drops into the vessel c. As soon as all the air has been expelled from K, the lower half of the tube fills with mercury to a height corresponding to the atmospheric pressure. The vessel c also fills. At this point remove from a the rubber tubing that leads to the source of

[1] Apparatus of M. Gony.

the suction and collect the dropping mercury in a flask.

To protect the flask *K*, wrap the lower half with wire gauze *D* and cover the upper half with a loose asbestos cap.

Errors Due to Temperature and Pressure Changes

From the equation on p. 671 it follows that a change of 1° in temperature on the Centigrade scale causes an error of about 0.37 ml on a volume of 100 ml of gas. A change greater than this may result from a change in room temperature or from the burning of combustible gases in the explosion pipet. It is necessary, therefore, in accurate work either to correct each reading or to maintain a constant temperature by enclosing the gas buret in a water mantle of about twice its size. The specific heat of a gas is small compared with that of water, and this water jacket is effective if the temperature of the laboratory is constant. This is more likely to be the case today with the heating of buildings controlled by thermostats. In routine work, when the analysis is started with the water in the jacket at room temperature, and the analysis is finished in less than an hour, the water jacket serves to prevent errors due to expansion or contraction of the measured gas by temperature changes and also to prevent error arising from the fact that the tension of water vapor varies with the temperature. This is *important if the gas is measured over water.*

A change of about 25 mm in the barometer reading, which is about the maximum variation under ordinary weather causes a change in a gas volume of about 3 33 per cent. Rarely does the barometer change more than 4 mm in an hour, but this can cause an error of about 0 5 per cent This error is prevented by attaching a compensating de-
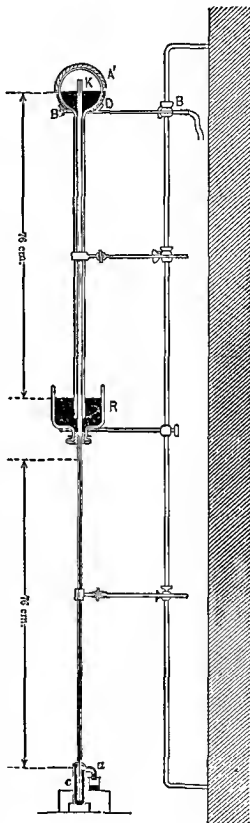
Fig. 106.

vice to the buret so that all the readings are made under a definite pressure which is independent of the barometer reading (cf. p. 330).

Errors Due to the Solubility of Gases in Confining Fluids

Pure water is impracticable as a confining fluid because of its solvent effect, which varies greatly with different gases An aqueous solution of sodium sulfate in 1.8 N sulfuric acid or a saturated solution of sodium chloride in 0.25 N hydrochloric acid is much better, and the addition of a little methyl orange colors the solution and makes it easier to read the meniscus. Mercury does not dissolve gases, but, as stated on p. 671, some of the reagents and some gases react with it. The following table shows the approximate number of milliliters of gas, under normal barometer readings, dissolved by 100 ml of water at 0° and at 20°. Increase of pressure causes a proportional increase in the solubility of a gas which does not react chemically with the liquid, and increase in temperature always lessens the solubility of the gas.

Kind of Gas	Milliliters Dissolved by 100 ml Water at 0°	Milliliters Dissolved by 100 ml Water at 20°
Acetylene, C_2H_2	173	103
Carbon dioxide, CO_2	171	83.0
Carbon monoxide, CO	3.5	2.3
Cyanogen, C_2N_2	550	450
Ethane, C_2H_6	9.87	4.72
Ethylene, C_2H_4	22.6	12.2
Hydrogen, H_2	2.1	1.8
Hydrogen sulfide, H_2S	468.6	267.0
Methane, CH_4	5.6	3.31
Nitrogen, N_2	2.4	1.5
Oxygen, O_2	4.9	3.1
Sulfur dioxide, SO_2	7979	3937

The solubility of a gas in a mixture of gases is less because the pressure exerted by all the gases present is equal to the atmospheric pressure and the solubility of each gas is proportional to its own partial pressure. The solubilities of the gases in the above-mentioned salt solutions is much less and the error due to solubility can be corrected by saturating the confining liquid with the gas (cf. p. 672).

Errors Due to Variations in Molecular Volumes

In ordinary calculations, students are taught that the molar volume of a gas at 0° and 760 mm pressure is theoretically 22 41 liters. For accurate work, such an assumption cannot be made. Thus, while the accurate values for the molar volumes of hydrogen, oxygen, and carbon monoxide are 22.41, 22.39, and 22.40 liters respectively, the value for methane is 22.36 and for carbon dioxide it is 22 26. Thus, the burning of 100 ml of carbon monoxide will only yield 99.5 ml of carbon dioxide and, from the equation $CO + O_2 = CO_2$, it is assumed that the volume of CO_2 formed is exactly equal to the volume of CO, provided that the temperature and constant, an error of 0.5 per cent will be made (cf

Subdivisions of Gas Analysis

According to the manner of determining the amount of gas, a distinction is made between:

1. *Absorption Methods.*
2. *Combustion Methods.*
3. *Titrimetric Methods.*

Some gases, such as argon, neon, helium, and mixtures of some hydrocarbons, can be determined only mechanically as by liquefaction and fractional distillation, by dissolving in a liquid, or by freezing.

In an *absorption method* the mixture of gases is treated with a series of absorbents. The difference in the volumes of the gas before and after it has been acted upon by each absorbent represents the amount of gas absorbed. The absorption of the gas may take place in the measuring tube itself, or better, in separate absorption vessels.

In this way, the amount of carbon dioxide, heavy hydrocarbons (ethylene, benzene, acetylene, etc.), oxygen, and carbon monoxide may be determined in illuminating gas, producer gas, water gas, or Dowson gas.

After the constituents capable of absorption have been removed, a gas residue is left consisting of hydrogen, methane, and nitrogen; the first two constituents are determined by combustion; the last is always determined by subtracting the total amount of other gases found from 100 per cent.

For a *combustion analysis* the unabsorbed constituents of the gas mixture are mixed with air, or oxygen, in more than sufficient amount to ensure complete combustion, and burnt in a suitable apparatus; the amount of combustible gas is determined by measuring the contraction, the amount of carbon dioxide formed, and the excess of oxygen.

Finally, if the gas evolved by means of a chemical reaction is measured, and from the volume of the gas the weight of the body producing it is calculated, we have made use of what is called a *gas-volumetric* method. (Cf. "Determination of Carbonic and Nitric Acids," pp. 329 and 386.)

CHAPTER XIX

DETERMINATION OF SOME COMMON GASES

1. Carbon Dioxide, CO_2. Mol. Wt. 44.01

Density = 1.5290[1] (air = 1).   Weight of 1 l = 1.976 g
Molar volume = 22.26 l.   Critical temperature = +31.5°C

Carbon dioxide is absorbed to a considerable extent by water; 1 vol. water absorbs: at 0°, 1.7967 ml CO_2; at 15°, 1.0003 ml CO_2; at 25°, 0.8843 ml CO_2, or in general[2]

$$\beta = 1.7967 - 0.07761 \times t + 0.0016424 \times t^2$$

Absorbents. When it is desired to determine only CO_2 in a gas mixture, the use of a solid absorbent such as Ascarite (cf. p. 325) is best, and in such cases the determination is based on the gain in weight of the tube containing the absorbent. In technical gas analysis, however, solutions of potassium hydroxide, sodium hydroxide, or barium hydroxide are used.

Potassium Hydroxide. Dissolve 360 g of pure, electrolytic potassium hydroxide in about 500 ml of water and dilute to 1 l.

During the last fifty years probably potassium hydroxide has been used more than any other reagent for absorbing CO_2. In combustion analysis (pp. 344, 354) the use of a solid absorbent is now preferred although some chemists still use a weighed bulb containing potassium hydroxide solution. In ordinary gas analysis, the gas can be passed through the absorbent, back and forth, several times, but in combustion work the gas goes through the apparatus only once. When a Geissler tube (p. 355) is used the gas must pass through it quite slowly and

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[1] This number is the mean from the observations of Lord Rayleigh (1897) = 1.52909, Leduc (1898) = 1.52874, and Christie (1905) = 1.52930.

[2] β is called the *absorption coefficient of the gas.* This signifies the *volume* of gas, measured at 0° and 760 mm pressure, which 1 ml of a liquid at $t°$ will absorb when the pressure upon the surface of the liquid is 760 mm. If h ml of liquid, at $t°$ and B mm pressure, absorbs V ml of the gas, then the absorption coefficient can be computed by the equation: $\beta = \dfrac{V}{h(1 + \alpha t)}$:

there is likely to be some loss of moisture escaping through the small drying tube at the exit end of the tube. With a dry absorbent in a tube fitted with capillary entrance and exit tubes, the gas can be absorbed much more rapidly and the loss of moisture easily prevented. One milliliter of the potassium hydroxide solution prepared as just described can be expected to absorb efficiently at least 30 ml of CO_2 (about 0.15 g) measured at room temperature and pressure of 1 atmosphere.

Sodium Hydroxide. Dissolve 315 g of pure electrolytic sodium hydroxide in water and dilute to 1 l. Potassium hydroxide has been preferred by many chemists because $KHCO_3$ is more soluble in the alkaline solution than $NaHCO_3$ is and consequently can be used to absorb more CO_2 without any solid separating. Sodium hydroxide is cheaper, and its solutions do not have a tendency to foam when gas is bubbled through them. The two solutions are equally efficient.

Barium Hydroxide. When the CO_2 content of a gas mixture is small, as in air, some chemists prefer to use barium hydroxide solution. Thus, in air analysis, a large sample of air can be shaken with a small volume of standardized $Ba(OH)_2$ and the determination based on the titration of the unneutralized base to a phenolphthalein end point (cf. pp. 498, 521).

If the gas analyzed contains other constituents of an acid nature such as SO_2, H_2S, HCN, or $(CN)_2$, they should be removed before any attempt to determine the CO_2 or they will also be absorbed by the above-mentioned solutions. The caustic alkali solutions also absorb some of the *illuminants*, particularly C_6H_6, until they have become saturated with them.

2. Carbonyl Sulfide, COS. Mol. Wt. 60.07

Density = 2.0999 (air = 1)   Weight of 1 l = 2715 g.   Molar volume = 22.13 l.
Boiling point −47.5°.   Density of liquid COS, 1 0601.   Critical temperature, between 91° and 102°
Vapor pressure of liquid COS in atmospheres: 0° = 14 5, 5° = 17 4, 22 8° = 20.3, 41° = 28 1, 67° = 36.7, 74° = 48.4, 91° = 62 9, 102° = ∞.

Carbonyl sulfide is colorless, odorless, and tasteless. It shows the following behavior toward reagents:

1. *Water* absorbs an equal volume of gas at ordinary temperatures. The solution is odorless and tasteless at first but soon hydrolyzes slightly: $COS + H_2O = CO_2 + H_2S$.

2. *Dilute caustic potash* solution does not absorb COS much better than water does. *Concentrated caustic potash* solution absorbs it, forming potassium carbonate and sulfide: $COS + 4KOH = K_2CO_3 + K_2S$

$+ 2H_2O$. The absorption is so slow that COS can be freed from CO_2 and H_2S by washing with potassium hydroxide solution. Alcoholic caustic potash absorbs COS quickly and completely.

3. *Ammonia.* Concentrated ammonium hydroxide solution absorbs COS slowly but completely, forming ammonium thiocarbamate: $COS + 2NH_3 = NH_2COSNH_4$, and, in the presence of hydrogen peroxide, sulfate and carbonate are formed:

$$COS + 4H_2O_2 + 4NH_3 = (NH_4)_2SO_4 + (NH_4)_2CO_3 + 2H_2O$$
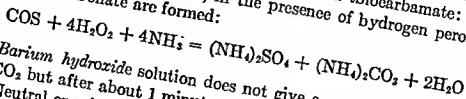
4. *Barium hydroxide* solution does not give a precipitate at once as with CO_2 but after about 1 minute a turbidity results.

5. Neutral or acid solutions of *silver nitrate* or *lead acetate* do not give precipitates of sulfide for about 8 minutes. In an ammoniacal solution of silver or zinc, or in a caustic alkali solution of lead salt, a precipitate of sulfide is formed immediately.

6. *Copper sulfate* in acid solution absorbs almost no COS.

7. *Iodine* in neutral or alkaline solution has very little oxidizing effect. Chlorine and bromine act only slightly at ordinary temperatures.

8. *Bromine* in alkaline solutions oxidizes COS readily: $COS + 4Br_2 + 12KOH = K_2CO_3 + K_2SO_4 + 8KBr + 6H_2O$.

9. *Fuming sulfuric acid* absorbs COS at room temperature without much oxidation; on being heated, sulfuric acid and CO_2 are formed.

10. *Triethyl phosphine* does not absorb COS (difference from CS_2).

11. *Palladous chloride* absorbs COS quickly and quantitatively at 40–50°: $PdCl_2 + COS + H_2O = 2HCl + CO_2 + PdS$.

12. Mixed with 1.5 volumes of oxygen, COS burns with explosive violence and blinding light. In contact with glowing platinum COS decomposes smoothly into CO and S without change in volume.

Determination of Carbonyl Sulfide

1. Determination of COS and CO_2 in the Presence of Each Other

Absorb the two gases in an ammoniacal solution of calcium chloride. Add neutral hydrogen peroxide, boil, filter off the calcium carbonate, carefully avoiding contamination from the carbon dioxide in the air, wash with hot water, dissolve in T ml of $0.1 N$ hydrochloric acid, and titrate back with $0.1 N$ sodium hydroxide solution (p. 500). The difference $T - t$ multiplied by 1.113 gives the milliliters of the original CO_2 (at 0° and 760 mm) together with that formed from the COS. Evaporate the filtrate to small volume, make acid with hydrochloric acid, and determine the sulfuric acid as barium sulfate (p. 396). If the weight of $BaSO_4$ is p g then $94.8 p$ ml of COS was present, measured under stand-

ard conditions. It may be assumed, without serious error, that an equal volume of CO_2 was formed from it.

The absorption reaction is:

$$COS + 4H_2O_2 + Ca + 4NH_3 \rightarrow CaCO_3 + SO_4^{--} + 4NH_4^+ + 2H_2O$$

The CO_2 originally present is

$$(T - t)1.113 - 94.8\,p = ml\ CO_2\ at\ 0°\ and\ 760\ mm$$

Remark. This method of analysis is suitable for the determination of large quantities of COS and CO_2. If but little COS is present mixed with considerable CO_2, Dede[1] recommends passing 25 l of the gas through palladous chloride solution heated to 50°. The COS is decomposed quantitatively into an equivalent quantity of PdS. Filter off the precipitate, dissolve it in hydrochloric acid and potassium chlorate, and determine the sulfur as barium sulfate.

2. Determination of COS, H_2S, and CO_2 in a Mixture

First determine the hydrogen sulfide content by bubbling the gas through a measured volume of 0.1 N iodine solution until it is nearly decolorized. Determine the excess of iodine by titration with sodium thiosulfate solution. If t ml of 0.1 N iodine was used in reaction with H_2S, then 1.108 t ml of H_2S was present, measured under standard conditions. This corresponds to 0.01167 t g $BaSO_4$.

In a second equally large volume of the gas absorb the three gases in an ammoniacal solution of calcium chloride. Afterwards boil with hydrogen peroxide and continue the analysis as in method A. Assume that t_1 ml of 0.1 N acid was neutralized by the calcium carbonate and that p g of $BaSO_4$ was formed. Then

$$COS = (p - t \times 0.01167)94.8\ ml\ at\ 0°\ and\ 760\ mm$$

$$CO_2 = t_1 \times 1.113 - (p - t \times 0.01167)94.8\ ml\ at\ 0°\ and\ 760\ mm$$

The Heavy Hydrocarbons (Illuminants)

Ethylene (Ethene), C_2H_4; Benzene, C_6H_6; Acetylene (Ethine), C_2H_2

3. Ethylene,[2] C_2H_4. Mol. Wt. 28.05

Density = 0 9738 (air = 1)   Weight of 1 l = 1.256 g[3]
Molar volume = 22.27.   Critical temperature = +9°C

[1] Chem. Ztg, 1914, 1075
[2] And its homologs.
[3] T. Batuecas, Helv. Chim Acta, 1, 136 (1915).

Absorption Coefficient for Water

One volume of water absorbs at $0°$ 0.256 ml C_2H_4; at $15°$, 0.161 ml C_2H_4; at $20°$, 0.149 ml C_2H_4; or in general, $\beta = 0.2563 - 0.009136t + 0.0001881t^2$.

Alcohol absorbs more ethylene; the general formula is $\beta = 3.5945 - 0.07716 \cdot t + 0.0006812 \cdot t^2$.

Absorbents. *Fuming sulfuric acid* (with 20–25 per cent free SO_3) also called *oleum* (cf. p. 509), is used when no separation of the illuminants is desired. It can be purchased or prepared by heating concentrated sulfuric acid and passing the fumes into a cooled receiver containing concentrated sulfuric acid. It is really a mixture of H_2SO_4 and pyrosulfuric acid, $H_2S_2O_7$, although the analyst usually regards it merely as a solution of SO_3 in H_2SO_4. Pyrosulfuric acid is a well-defined chemical compound which melts at $35°$. Ethylene reacts with fuming sulfuric acid to form ethyl sulfuric acid, $C_2H_5SO_4H$, and ethyl pyrosulfuric acid, $C_2H_5S_2O_7H$.

Fuming sulfuric acid absorbs the higher hydrocarbons of the methane series probably without chemical combination. It absorbs benzene, C_6H_6, to form benzene sulfonic acid, $C_6H_5SO_3H$, and acetylene to form acetylene sulfate, $C_2H_4SO_4$. By prolonged contact it also absorbs some ethane, C_2H_6, but in ordinary practice the quantity is negligible. When a gas is passed through fuming sulfuric acid, the unabsorbed gas always carries SO_3 fumes away with it; these must be absorbed by the caustic potash pipet before measuring the unabsorbed gas residue.

Bromine. A saturated solution of bromine in 5 per cent potassium bromide solution can be used for absorbing the illuminants, but it is not suitable for use in gas pipets. It reacts with ethylene to form ethylene dibromide, $C_2H_4Br_2$, and with propylene to form propylene dibromide, $C_3H_6Br_2$. With benzene it forms bromobenzene, but it does not absorb benzene as well as fuming sulfuric acid does and the bromination probably does not stop at the monosubstitution product. An aqueous solution of bromine can also be used for absorbing ethylene. If the concentration of the solution is known the excess can be measured by titrating iodimetrically after the absorption. This is an excellent method for determining ethylene in the presence of benzene.

Palladous Chloride. A 0.5 to 1.0 per cent solution of $PdCl_2$ is reduced to palladium by carbon monoxide or by ethylene and its homologs.

$$PdCl_2 + CO + H_2O = 2HCl + Pd + CO_2$$

$$PdCl_2 + C_2H_4 = C_2H_4Cl_2 + Pd$$
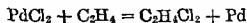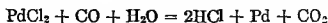
The precipitate of palladium black is easily recognized, and it is possible to detect 0.2 per cent ethylene when 100 ml of a gas mixture is slowly passed through 30 to 40 ml of $PdCl_2$. The solution is not suitable for use in pipets, but the test is excellent for qualitative purposes. Hydrogen, however, also reacts slowly with the reagent.

The best method for separating the individual illuminants involves fractional distillation. The Bureau of Mines, however, has successfully used sulfuric acid of different strengths in the presence of nickel and silver sulfates for separating ethylene, propylene, and butylene in the absence of carbon monoxide. Passing the gas through sulfuric acid of different densities also effects a rough separation in the absence of catalyzers. Ammoniacal cuprous chloride solution will also absorb ethylene.

4. Benzene, C_6H_6. Mol. Wt. 78.11

Benzene is a liquid which boils at 80.1°. To the extent that it is present as gas, it can be assumed that the molar volume is 22.39 l.

Benzene is readily soluble in alcohol, ether, carbon bisulfide, caoutchouc, ethylene bromide, bromine, and fuming sulfuric acid.

Absorbents. *Fuming sulfuric acid*[1] and *bromine water containing an excess of bromine.* After the solution has been used once, the absorption is incomplete.

Inasmuch as benzene is neither brominated nor oxidized by bromine at ordinary temperatures, it was difficult to understand why bromine water should absorb it quantitatively. In fact, Berthelot[2] and Cl. Winkler[3] disputed it, but the results of Treadwell and Stokes[4] have been confirmed by Haber. Haber suggested that the absorption of benzene by bromine was of a purely physical nature, and M. Korbuly[5] has shown this to be true. Just as bromine can be removed from aqueous solution by shaking with benzene, so benzene can be removed by shaking with bromine, or even ethylene bromide and like solvents.

By means of highly concentrated nitric acid (d 1.52) benzene is also absorbed; this solvent cannot be used in the analysis of gases containing carbon monoxide, for this gas is quantitatively oxidized to carbon dioxide by nitric acid of this strength, and is therefore removed with the benzene when the acid vapors are neutralized by caustic potash solution.

[1] Benzene sulfonic acid is formed, $C_6H_5SO_3$

[2] Compt. rend., 83, 1255

[3] Z. anal. Chem., 1889, p. 284.

[4] Treadwell and Stokes, loc. cit.

[5] Inaug. Dissertation, Zürich, 1902

[6] Treadwell and Stokes, Ber., 21, 3131 (1888).

Behavior of Benzene to Water

Benzene vapors are absorbed to a considerable extent by water and all aqueous salt solutions, a circumstance which must be considered when an exact gas analysis is to be made. To determine how much benzene is absorbed by water, M. Korbuly performed the following experiments:

Different amounts of air containing 3.16 per cent of benzene vapor were shaken in a Drehschmidt's pipet with the same amount of water (5 ml) until no more benzene was absorbed. He obtained the following results:

Experiment	Gas Taken, ml	Per Cent Benzene Present by Volume	Percentage of Benzene Absorbed at the End of 3 Minutes
1	58.92	3.16	1.28 ml = 2.17
2	61.14	3.16	0.80 ml = 1.31
3	53.32	3.16	0.52 ml = 0.89
4	50.86	3.16	0.44 ml = 0.73
5	60.78	3.16	0.28 ml = 0.46
6	59.88	3.16	0.08 ml = 0.01
7	60.20	3.16	0.02 ml = 0.00

Potassium hydroxide behaves similarly.

In the analysis of a mixture of carbon dioxide and benzene, it is customary first to remove the carbon dioxide by means of potassium hydroxide solution and then the benzene with fuming sulfuric acid or bromine. It is evident, then, that both of the results obtained will be inaccurate if a fresh solution of potassium hydroxide is used for the absorption of the carbon dioxide, for this will absorb not only the whole of the carbon dioxide, but in many cases nearly all the benzene. Accurate results may be obtained by using a solution of potassium hydroxide which has been saturated with benzene vapors.

5. Acetylene, C_2H_2. Mol. Wt. 26.04

Density = 0.0087 (air = 1).[1]   Weight of 1 l = 1.175 g
Molar volume = 22.03 l.   Critical temperature = $+37°C$
Boiling point = $-80.6°C$

Acetylene is quite soluble in water; 1 volume of water at the ordinary temperature absorbs an equal volume of this gas. In amyl alcohol,

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[1] M. Bretscher (Inaug. Dissert., Zürich, 1011), M. Stahrfoss and P. A. Guye (Arch. sci. phys. nat., 28, 1909). The mean of their two values is used.

chloroform, benzene, glacial acetic acid, and acetone it is much more soluble; thus 1 volume of acetone absorbs 31 volumes of acetylene.[1]

Absorbents. *Fuming sulfuric acid.*[2] By saturated *bromine water,* acetylene is absorbed rapidly in the cold, but 0.1 N bromine water containing hydrochloric acid absorbs acetylene so slowly that it permits the titration of ethylene in the presence of acetylene (see p. 737).

By means of ammoniacal cuprous chloride, acetylene is absorbed and forms red copper acetylide $Cu - C \equiv C - Cu$. This reaction is so characteristic that it is used for the

Qualitative Detection of Acetylene

in gas mixtures. This test is best performed by the method of L. Ilosvay von Nagy Ilosva.[3]

Preparation of the Reagent. Place 1 g of copper nitrate (chloride or sulfate) in a 50-ml measuring flask and dissolve in a little water. To the solution, add 4 ml of concentrated ammonia (20–21 per cent NH_3) and 3 g of hydroxylamine hydrochloride. Shake the liquid until it becomes colorless, and immediately dilute with water up to the mark.

The Qualitative Test. Place a little of the reagent in a 500-ml glass-stoppered cylinder and pass the gas to be tested for acetylene (illuminating gas) over it until the color of the reagent becomes pink. Stopper the cylinder and shake. If acetylene is present, a beautiful red precipitate is immediately formed. Another method of making the test is to pass the gas through a small bulb tube containing glass wool moistened with the reagent.

The above qualitative test can be used for the colorimetric determination of as little as 0.03 mg of C_2H_2 in gases. It is necessary then to add a protective colloid, such as glue, to the reagent so that the copper acetylide does not precipitate but remains in red colloidal solution.

The test can also be carried out as follows:

Determination of Acetylene in Gases.[4] Pass a measured volume of the gas through 30 ml of fresh ammoniacal cuprous chloride (prepared as described below) contained in a suitable bubble tube. Filter off the red copper acetylide precipitate and wash it with very dilute ammonia solution until the washings are colorless. Dissolve the precipitate by pouring a little 6 N hydrochloric acid through the filter, and wash with water. Save the solution. To recover a little undissolved copper,

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[1] Hempel, *Gasanalytische Methoden.*

[2] $C_2H_2SO_4$ is formed.

[3] *Ber*, **32**, 2698 (1899).

[4] *Methods of the Chemists of the U. S. Steel Corporation.*

ignite the filter in a porcelain crucible, digest the ash with 2 drops of concentrated nitric acid, and wash the solution into the beaker containing the main solution. Determine the copper content by any good method. $2Cu = 1C_2H_2$.

Preparation of the Reagent. Pour a solution containing 22.5 g Cu_2Cl_2, 180 ml of concentrated HCl, and water to make 300 ml into 4 l of water. Allow the Cu_2Cl_2 precipitate to settle, decant off the supernatant solution, and transfer the remaining solution and precipitate to a graduated 250-ml cylinder. After 2 hours, siphon off the liquid, together with some precipitate, down to the 50-ml mark, and add 4 N NH_3 solution to the 230-ml mark. Shake well, allow to stand several hours, transfer to glass-stoppered tubes containing several pieces of fine copper wire, and keep closed until ready for use.

Separation of the Heavy Hydrocarbons from One Another

The separation of ethylene, propylene, and butylene was discussed briefly on p. 693. For separating ethylene and benzene, Haber and Oechelhäuser have devised a method which is accurate and to be recommended.

Principle. In one portion of the gas, the sum of the ethylene and benzene is determined by absorption with bromine water or fuming sulfuric acid, while in a second portion the gases are absorbed in titrated bromine water, and the excess of the latter is determined iodimetrically. From the amount of bromine required the ethylene is calculated:

$$1 \text{ ml } 0.1 \text{ } N \text{ I} = 1.113 \text{ ml } C_2H_4 \text{ at } 0°C \text{ and } 760 \text{ mm pressure}$$

As this analysis is often performed in the Bunte buret, it will not be explained in detail until this has been described. (See p. 737.)

The acetylene used in industrial plants is purchased in cylinders which contain a solution of the gas in acetone, CH_3COCH_3, under a pressure of 10 to 12 atmospheres. Under this pressure, acetone absorbs about 100 times its own volume of the gas. As the gas is used, some acetone vapor escapes with the acetylene. If it is desired to analyze the gas, it must be collected over mercury as both acetone and acetylene are very soluble in water. The analysis is made by absorbing both acetone and acetylene in fuming sulfuric acid and examining the residue for oxygen, hydrogen, methane, and air.

6. Oxygen, O = 16. Mol. Wt. 32

Density = 1.0153 (air = 1). Weight of 1 l = 1.4289 g
Molar volume = 22.39 L   Critical temperature = −119°C

Oxygen is only slightly soluble in water; according to the experiments of L. W. Winkler,[1] 1 l of water will absorb the following quantities of oxygen, nitrogen, and air at 760 mm pressure:

[1] *Ber.*, **34**, 1410 (1901).

ABSORPTION OF ATMOSPHERIC AIR IN WATER

Temperature	Oxygen	Nitrogen	Air
	ml	ml	ml
0°............	10.24	18.57	28.81
5°............	8.98	16.45	25.43
10°..........	7.97	14.67	22.64
15°..........	7.16	13.29	20.45
20°..........	6.50	12 19	18.69
25°..........	5.93	11.31	17.24
30°..........	5.47	10 59	16.06
35°..........	5.11	9 92	15.03
40°..........	4.83	9.35	14.18
45°	4.58	8.93	13.51
50°.	4.38	8.59	12.97
55°..........	4.22	8.31	12.53

From these data, the absorption coefficient of pure oxygen for water at 0-55° can be computed.

ABSORPTION COEFFICIENTS OF OXYGEN FOR WATER

Temperature	β	Temperature	β
0°..... .. .	0 04890	30°....	0.02608
5°.	0 04286	35°.	0.02440
10°.	0 03802	40°............	0 02306
15°. ..	0.03415	45°............	0 02187
20°	0 03102	50°...	0.02090
25°.	0 02831	55°	0.02012

Oxygen can be determined by combustion or by absorption.

Determination of Oxygen by Combustion

The determination of oxygen by combustion may be effected by exploding it with hydrogen (Bunsen) or by conducting a mixture of the two gases through a glowing platinum capillary (Drehschmidt), exactly as in the determination of carbon monoxide (cf. p. 704). In both cases the combustion takes place in accordance with the equation:

$$O_2 + 2H_2 = H_2O$$
1 vol.   2 vols.   0 vol.
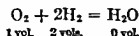
Three volumes of gas, therefore, disappear for each volume of oxygen present (cf. p. 686). If the contraction resulting from the combustion

of a mixture of oxygen and an excess of hydrogen is designated by V_{C_1}, then the amount of oxygen present $= \frac{1}{3}V_{C_1}$.

Determination of Oxygen by Absorption

The reagents commonly used for absorbing oxygen are: (1) a strongly alkaline solution of sodium or potassium pyrogallate, and (2) yellow phosphorus sticks. (3) Chromous chloride, $CrCl_2$, solution is the most rapid absorbent and for some purposes the most accurate. (4) Hot copper or an ammoniacal of ammonium carbonate containing rolls of copper gauze is also effective. (5) A solution of 50 g sodium hyposulfite, $Na_2S_2O_4$, in 250 ml of 4.8 N KOH in the Hempel huret or of 10 g $Na_2S_2O_4$ in 1.35 N NaOH in the Bunte huret has been recommended. With sodium hyposulfite, the absorption is always complete within 5 minutes. (6) Manganous hydroxide has also been recommended.

Potassium Pyrogallate Solution. Prepare a stock solution of potassium hydroxide by dissolving 600 g of electrolytic KOH in water and diluting to 1 l. Caustic alkalies purified with alcohol should not be used in preparing reagents for the absorption of oxygen, for their solutions evolve some carbon monoxide. Prepare also a stock solution of pyrogallol (1,2,3-trihydroxybenzene = $C_6H_3(OH)_3$) by dissolving 300 g of this trihydroxy phenol (sometimes called pyrogallic acid) in 800 ml of water and diluting to 1 l. To prepare the reagent for use, mix 40–50 ml of the stock pyrogallol solution with 3.5 times as much of the stock potassium hydroxide solution. Mix thoroughly, and keep in a stoppered vessel to avoid too much contact with air.

Sodium Pyrogallate Solution. Mix 60 to 65 of the stock pyrogallol solution (see above) with 2.5 times as much of 50 per cent sodium hydroxide solution.

Both these alkaline pyrogallate solutions absorb oxygen quite rapidly when fresh. After each milliliter of reagent has absorbed 8 to 10 ml of oxygen it reacts more slowly and should not be used much longer. The absorption is slow at low temperatures and appears to be most favorable at about 20°.

Yellow Phosphorus. The absorption of oxygen by means of phosphorus takes place by simply allowing the gas containing the oxygen to remain over moist phosphorus. The formation of white clouds indicates the presence of oxygen, and their disappearance shows that the absorption is complete. A temperature of 15–20° is best suited for the absorption.

The oxygen is completely absorbed at the end of 3 minutes from 100 ml of air at this temperature. At lower temperatures the

absorption requires more time, and at 0° more than an hour is necessary.

If the gas contains more than 60 per cent of oxygen, moist phosphorus will absorb none of it at the ordinary atmospheric pressures. In this case the gas must be diluted with nitrogen or hydrogen until a mixture is obtained containing less than 60 per cent oxygen, or the gas must be allowed to act upon the moist phosphorus under diminished pressure. In the latter case, however, the phosphorus easily becomes heated enough to melt and the reaction becomes too violent.

Oxygen is not absorbed by moist phosphorus if the gas contains traces of heavy hydrocarbons, ethereal oils, alcohol, or ammonia. According to Hempel[1] 0.04 per cent of ethylene, and according to Haber[2] 0.17 per cent, suffices to prevent completely the absorption of oxygen.

The yellow phosphorus should be used in the form of small sticks of 4- to 6-mm diameter. To prepare the sticks, place some yellow phosphorus under water in a test tube. Place the tube in a water bath at about 50° to melt the phosphorus. Push a glass tube of the proper diameter into the molten phosphorus and suck up the phosphorus to the desired height. Then withdraw the tube and place it in cold water. Push out the solidified phosphorus into the reagent pipet which also contains water. Cover the chamber of the pipet with black paper to protect the phosphorus from light, which converts it into the red modification. When, in using the pipet, the white fumes that develop are very slowly or incompletely absorbed in 1 or 2 minutes, renew the supply of phosphorus.

The phosphorus is not easy to handle, and it cannot be used for mixtures rich in oxygen because the heat of the reaction is likely to melt the phosphorus and fuse it into a solid mass. Its action is slow at temperatures below 15° and with gases containing considerable methane or ethane.

Chromous Chloride. Although this reagent is one of the most rapid absorbents for oxygen and has been in use for nearly 50 years, it has not been very popular because it is difficult to prepare and keep in the reduced state. Stable solutions in quantities sufficient to charge a pipet can be prepared best by reducing chromic chloride in a Jones reductor (p. 544) containing amalgamated zinc. Dissolve 75 g $CrCl_3$ in 190 ml of water and 10 ml of concentrated HCl. Pour the solution into the funnel tube of the reductor, which is charged with amalgamated zinc and filled with water, until the water at the bottom of the reductor becomes colored. Then attach the bottom of the reductor, by means of a rubber stopper carrying a small Bunsen valve (p. 540), to the rear chamber of a pipet filled with coke-oven gas, natural gas, or some other

[1] *Gasanalytische Methoden.*

[2] *Experimental-Untersuchungen über Zersetzungen und Verbrennungen von Kohlenwasserstoffen,* Habilitationsschrift, Munich, 1896.

gas free from oxygen, and allow the rest of the chromic chloride solution to run into the pipet dropwise until the proper level has been reached. At once connect the pipet to the rest of the apparatus and carefully protect the solution from the air. This solution will absorb all the oxygen in air bubbled through it from 2 to 4 times. It does not reduce H_2S, CO_2, or similar gases.

Manganous Hydroxide. This reagent has been used successfully since 1894 for absorbing small quantities of oxygen in *natural gas* and in other cases where the use of phosphorus is objectionable. The $Mn(OH)_2$ is nearly white when freshly prepared from manganous chloride and sodium hydroxide but becomes brown when manganic hydroxide is formed by the action of oxygen. The extent of the oxidation is determined iodimetrically.

$$4Mn(OH)_2 + O_2 + H_2O = 4Mn(OH)_3$$

$$2Mn(OH)_3 + 2I^- + 6H^+ = 2Mn^{++} + I_2 + 6H_2O$$

$$I_2 + 2S_2O_3^{--} = 2I^- + S_4O_6^{--}$$
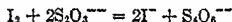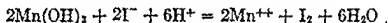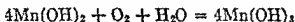
To carry out an analysis, fill a 150-ml Bunte buret with mercury and dmw in about 25 ml of 10 per cent $MnCl_2$ solution over the mercury. Rinse out the cup of the buret and add about 15 ml of a 10 per cent solution of sodium hydroxide. Then introduce 100 ml of the gas sample, close all stopcocks and allow the mixture to stand for 15 minutes with frequent shaking. Then draw 10 ml of 10 per cent potassium iodide solution into the pipet and, after this, 15 to 20 ml of N H_2SO_4. Transfer the solution to a flask and titrate promptly with 0.1 N thiosulfate solution. One milliliter of 0.1 N $Na_2S_2O_3$ solution = 0.560 ml O_2 at 0° and 760 mm pressure.

Determination of Absorbed Oxygen in Water. Method of L. W. Winkler[1]

1000 ml 0.1 N $Na_2S_2O_3$ solution = $\dfrac{O}{20}$ = 0.8 g = 559.8 ml oxygen at 0° and 760 mm pressure

Principle. If water containing dissolved oxygen is heated in a closed vessel with manganese hydroxide, the latter is oxidized to manganous acid according to the following equation:

$$Mn(OH)_2 + O = H_2MnO_3$$
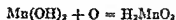
The amount of oxygen taken up is determined iodimetrically by adding hydrochloric acid and potassium iodide to the manganous acid and titrating the liberated iodine:

$$H_2MnO_3 + 4HCl = MnCl_2 + 2H_2O + Cl_2 \quad \text{and} \quad 2KI + Cl_2 = 2KCl + I_2$$
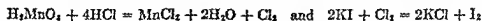
Reagents Required. 1. *An approximately 4 N $MnCl_2$ solution* obtained by dissolving 400 g of $MnCl_2·4H_2O$ in water and diluting to 1000 ml. The manganese chloride must be free from iron.

[1] *Ber.,* 21, 2843 (1888).

2. *Sodium Hydroxide Solution Containing Potassium Iodide.* On account of the nitrite usually present in commercial sodium hydroxide, prepare the solution from sodium carbonate and calcium hydroxide. Siphon off the clear liquid and concentrate in a silver dish until its density is 1.35. In 100 ml of this solution, dissolve 10 g of potassium iodide.

A portion of the alkaline potassium iodide solution on being acidified with hydrochloric acid should not immediately turn starch paste blue, and, furthermore, large amounts of carbonate must not be present.

3. *0.1 N Sodium Thiosulfate Solution.*

Procedure. Take a glass-stoppered flask of about 250-ml capacity and determine its exact capacity by weighing it first empty and then filled with water at 20°. If the water to be analyzed is saturated with air, simply pour it into the flask; otherwise conduct the water through it for 10 minutes. By means of a pipet reaching to the bottom of the flask, introduce 1 ml of the alkaline potassium iodide solution and immediately afterwards 1 ml of the manganese chloride solution. Stopper the flask, shake, and allow to stand until the precipitate has settled. Then, by means of the long-stemmed pipet, add about 3 ml of concentrated hydrochloric acid and once more shake the contents of the flask. The precipitate dissolves readily with liberation of iodine; titrate the iodine with sodium thiosulfate in the usual way.

Remark. The results obtained by this method agree closely with those obtained by boiling the water as described on p 678.

7. Carbon Monoxide, CO. Mol. Wt. 28.01

Density = 0.96702 (air = 1) Weight of 1 l = 1.2502 g
Molar volume = 22 397 l. Critical temperature = −136°C

ABSORPTION COEFFICIENTS OF CARBON MONOXIDE FOR WATER*

Temperature	β	Temperature	β
0°........	0.03537	30°............	0 01998
5°..........	0 03149	35°.....	0.01877
10°..........	0 02816	40°..........	0.01775
15°..........	0.02543	45°.......... .	0.01690
20°..........	0 02319	50°..........	0 01615
25°..........	0.02142	55°..........	0.01548

* L. W. Winkler, *Ber.*, 34, 1414 (1901).

In alcohol the gas is about 10 times more soluble than it is in water. Its determination is effected either by absorption or by combustion.

Absorbents. *Ammoniacal Cuprous Chloride.* Prepare a stock solution by dissolving 300 g of ammonium chloride and 270 g of pure Cu_2Cl_2 in water and diluting the solution to 1 l. To prevent oxidation place a few pieces of fine copper wire in the solution. When using, add ammonia until the white precipitate of basic copper hydroxide dissolves slowly on shaking. Avoid the use of too much ammonia; about 1 ml of concentrated ammonia solution is required for each 3 ml of stock solution.

The ammoniacal solution absorbs oxygen from the air and it is best not to add ammonia until the solution is to be used. Some ammonia is likely to be carried off with the unabsorbed gas and, for that reason, the gas should be passed through acid after the carbon monoxide has been absorbed.

Acid Cuprous Chloride Solution. Dissolve 75 g of pure cuprous chloride and 600 ml of concentrated hydrochloric acid in sufficient water to make 1 l.

The absorption of carbon monoxide by means of cuprous chloride takes place according to the equation:

$$Cu_2Cl_2 + 2CO \rightleftharpoons Cu_2Cl_2 \cdot 2CO \text{ [1]}$$

The compound $Cu_2Cl_2 \cdot 2CO$ is unstable and can be formed only when a certain pressure is exerted by the carbon monoxide, so that when the acid solution is used the absorption will never be quantitative. Further, if a gas free from carbon monoxide (nitrogen or hydrogen) is shaken with such a solution after it has been used several times, a part of the $Cu_2Cl_2 \cdot 2CO$ in solution will be decomposed according to the above equation in the direction of right to left, until the partial pressure of the carbon monoxide set free is sufficient to restore equilibrium. Consequently the volume of the gas will appear greater after it has been treated with the cuprous chloride solution than it was originally.

When an *ammoniacal* cuprous chloride solution is employed, the absorption of the carbon monoxide is almost quantitative, but after such a solution has been used repeatedly it will readily give up some of the gas, although not so readily as the solution of cuprous chloride in hydrochloric acid or calcium chloride.[2] It is advisable, therefore, to

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[1] The compound has been isolated in the solid state. According to W. A. Jones (*Am. Chem. J.*, 22, 287) its formula is $Cu_2Cl_2 \cdot 2CO \cdot 4H_2O$, but according to the experiments of C. v. Girsewald in the author's laboratory, the formula is $Cu_2Cl_2 \cdot 2CO \cdot 2H_2O$.

[2] Cuprous chloride is soluble in a concentrated solution of calcium chloride; 1 ml of this solution absorbs 12–15 ml of CO.

adopt the suggestion of Drehschmidt, and first absorb the greater part of the gas by means of an old solution of cuprous chloride, afterwards removing the last traces by means of a freshly prepared solution, or one which has been used but a few times.

Besides carbon monoxide, the ammoniacal cuprous chloride solution will absorb acetylene, ethylene, etc., so that these gases must be removed previously by means of fuming sulfuric acid or bromine water.

By long shaking with concentrated nitric acid (d 1.5), carbon monoxide is completely oxidized to carbon dioxide, which can be removed by treatment with potassium hydroxide solution.[1]

Cuprous Sulfate and β-Naphthol Mixture. M. Damiens[2] found that a suspension of cuprous oxide in strong sulfuric acid can be used for absorbing carbon monoxide, and Lebeau and Bedel found that the action is much improved by the addition of a phenol such as β-naphthol.

Add 200 ml of concentrated sulfuric acid to 25 ml of water and allow the diluted acid to cool. Place 20 g of pure cuprous oxide (prepared as described below) in a mortar and triturate it with the acid until all the oxide is in suspension. Then add the β-naphthol and triturate in the same way. Filter off unmixed particles of the naphthol by filtering through glass wool. Transfer to the absorption pipet, keep at a temperature above 15°, and protect from the light.

To prepare the cuprous oxide in a condition such that it forms a good suspension, dissolve 100 g of cupric acetate by heating with 1 l of water in a 2-l flask. Filter if necessary. Meanwhile dissolve 60 g of glucose in 400 ml of water and add this solution to the boiling cupric acetate solution. Boil until the blue color fades somewhat, allow to stand until the cuprous oxide has settled, filter, wash a few times with water and once with alcohol, and dry in a vacuum desiccator or, less suitably, in an oven at 90° to 100°.

The above cuprous oxide suspension absorbs CO to form $Cu_2SO_4 \cdot 2CO$, which is more stable than the corresponding chlorine compound. The mixture, prepared as above described, will absorb about 18 times its own volume of CO. For rapid work, two pipets can be used in series, one containing cuprous chloride and one containing cuprous oxide. Gases rich in CO should be treated first with the Cu_2Cl_2 reagent and then with the cuprous oxide suspension. This last reagent absorbs ethylene, propylene, butylene, some acetylene, and a little oxygen but does not absorb methane or its homologs, hydrogen, or nitrogen.

Determination of Carbon Monoxide by Combustion with Air or Oxygen

The following reaction shows how carbon monoxide may be determined by combustion: $2CO + O_2 = 2CO_2$.

$\quad\quad\quad\quad\quad\quad$ 2 vols. 1 vol. 2 vols.

[1] Treadwell and Stokes, *Ber.*, **21**, 3131 (1888).
[2] *The Gas World*, **82**, 101 (1925)

From the reaction it follows that:[1]

1. The difference in the volume of the gas mixture before and after the combustion is, for 2 volumes CO, $3 - 2 = 1$; and for 1 volume CO $= \frac{1}{2}$. This difference is designated as the contraction, V_c. The contraction caused by the combustion of carbon monoxide is, therefore, equal to half the original volume of CO.

2. The volume of the carbon dioxide formed is equal to the volume of the carbon monoxide originally present. If, then, the carbon dioxide is determined by absorption with caustic potash, the volume of the carbon monoxide is at once obtained, provided that no other combustible gas containing carbon is present at the same time.

3. For the combustion of 2 volumes of CO, 1 volume of oxygen is necessary, and consequently the amount of oxygen consumed is equal to half the volume of the carbon monoxide.

Methods of Effecting the Combustion

The combustion of the carbon monoxide can be carried out in several different ways: (1) by explosion; (2) by conducting the gas over glowing palladium or platinum; (3) by conducting the gas over copper oxide.
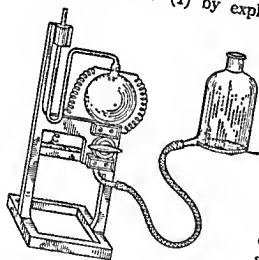
Fig. 107.

Combustion by Explosion. Mix the gas with a sufficient amount of air in a gas buret, and connect the buret by means of the capillary E with the Hempel's explosion pipet shown in Fig. 107. Drive over the gas into the pipet so that the capillary is entirely filled with mercury, close the stopcocks of the capillary and of the explosion pipet, and cause an electric spark to pass between the two platinum points which are fused into the glass walls of the pipet; this immediately causes an explosion to take place. Afterwards once more drive the gas back into the measuring buret, and again determine its volume. The difference in volume before and after the explosion represents the contraction.

This most excellent method can sometimes lead to erroneous results.

[1] These are molar volumes. Allowing for the difference in molar volumes, the equation reads:
44.79 l of CO react with 22.39 l of oxygen to form 44.52 l of CO_2 (cf. p. 715).

In practice, it is usually desired to determine the amount of combustible gas in a mixture containing nitrogen obtained after treatment with the different absorbents. If the amount of combustible gas present is too small in proportion to the amount of non-combustible gas, there will be no combustion whatsoever; on the other hand, if the relation is too large, a part of the nitrogen will be burnt to nitric acid (hydrogen is usually present). According to Bunsen, the combustion is complete when 30 volumes of combustible gas is present for each 2 volumes of non-combustible gas.

The combustion of carbon monoxide alone from a mixture of the same with hydrogen, methane, and air can be effected satisfactorily as follows:

After the gas has been freed from CO_2, unsaturated hydrocarbons and aqueous vapor, conduct it through a U-tube containing 0.7 g. pure iodine pentoxide[1] heated to 160°; by this means the carbon oxide is alone oxidized with liberation of iodine according to the equation $I_2O_5 + 5CO = 5CO_2 + I_2$.[3] If the gas is now conducted through Péligot tubes containing potassium iodide solution, the iodine is absorbed and can be titrated at the end of the experiment with sodium thiosulfate solution.

One milliliter 0.5 N $Na_2S_2O_3$ solution corresponds to 1 cc. CO measured under standard conditions.

If, after the carbon dioxide and water have once more been removed, the gas is passed through a combustion tube half filled with copper oxide and half with platinized asbestos, both heated to 300°, the hydrogen and methane will be completely burned to water and carbon dioxide, which can be absorbed and weighed as before. From the amounts of each, the hydrogen and methane present may be calculated.

8. Hydrogen, H. Mol. Wt. 2.016

Density = 0.0695 (air = 1). Weight of 1 l. .... g.
Molar volume = 22.4051. Critical temperature ....

Hydrogen is practically insoluble in water.

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[1] The U-tube is heated in a small paraffin bath.
[2] Iodine pentoxide is prepared by heating iodic acid at 150° until the water is completely removed.
[3] Nodzu, Comp. rend., 125, 70; Kremann, J. f. prakt.
Z. anorg. Chem., 60, 315; Kremann, J. anal. Chem.,
Z. anal. Chem., 54; Gerber and Nernst, ...,
L. Seidel and J. W. Nernst, Ber. deutsch. Bull., 45;
Gautier, Z. anal. Chem., 1888, 227.
[4] Lord Rayleigh, Proc. Roy. Soc., 42, 356.

ABSORPTION COEFFICIENTS OF HYDROGEN FOR WATER[*]

Temperature	β	Temperature	β
0°............	0.02148	30°............	0.01699
5°............	0.02044	35°............	0.01666
10°............	0.01955	40°............	0.01644
15°............	0.01883	45°............	0.01624
20°............	0.01819	50°............	0.01608
25°............	0.01754	55°............	0.01604

<small>[*] L. W. Winkler, *Ber.*, 24, 99 (1891).</small>

(a) Determination by Absorption. Method of Paal and Hartmann[1]

Colloidal palladium, in the presence of a protective colloid, sodium protalbinate, is capable of absorbing an enormous quantity of hydrogen. The absorption takes place slowly but quantitatively. The absorbent can be regenerated, after each experiment, by treatment with oxygen or by adding an easily reducible organic substance. Paal and Hartmann made use of sodium picrate for this purpose; the picric acid is reduced to triaminophenol:

$$C_6H_2(OH)(NO_2)_3 + 9H_2 = C_6H_2(OH)(NH_2)_3 + 6H_2O$$
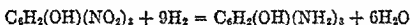
According to the experiments of Brunck[2] a solution of 2 g colloidal palladium and 5 g of picric acid dissolved in 22 ml of N sodium hydroxide diluted to 100–110 ml with water is a suitable absorbent. Such a solution can be purchased. The above quantity of reagent should absorb about 4 l of hydrogen; about 20–30 minutes, with repeated shaking, is required for the absorption. The reagent is useful for determining hydrogen in the presence of saturated hydrocarbons.

As soon as the efficiency of the absorbent is lost, rinse out the contents of the absorption pipet with water and add dilute sulfuric acid as long as any precipitate forms but avoid too much excess which tends to cause the palladium sol to go into solution as palladous sulfate, as a result of atmospheric oxidation. The precipitate of solid palladium and protalbinic acid also contains picric acid. Wash with water, which removes some of the acids but no palladium. Then suspend the mass in water and add sodium hydroxide solution, dropwise, until a colloidal solution is obtained. Finally add the proper quantity of sodium picrate and the absorbent is ready for use again.

[1] *Ber.*, 43, 243 (1910).

[2] *Chem. Ztg.*, 1910, 1313 and 1331.

Some chemists have had good results with palladiumized asbestos. To prepare this, dissolve 1 g of the metal in a small beaker with 2 ml of concentrated HNO_3 and 1 of concentrated HCl. Add the acid slowly while gently heating. Evaporate to dryness on the steam bath and dissolve the residual $PdCl_2$ in a very little water. Add 4 ml of a cold saturated solution of sodium formate, HCOONa, and make strongly basic by adding Na_2CO_3. Add about 1 g of soft, long-fiber asbestos, purified by heating strongly, treating with hydrochloric acid, washing, drying, and again heating at a low temperature. After the asbestos is well impregnated with the solution, dry it at 105°. Wash again with water to remove all sodium salts, and dry. Pack the dried asbestos in tubing of 10- to 12-cm length and 7.5- to 10-cm bore with capillary tubing of 1-mm bore fused to both ends. Fuse on the last end after the filling of the larger tubing. To determine hydrogen mix a measured volume of the gas, which has been freed from CO, with twice as much oxygen as is necessary to unite with the hydrogen to form water. Pass the mixture through the absorbent at a rate of about 15 ml per minute with its container heated to about 100° in a water bath. Pass the gas more slowly if the asbestos shows any signs of glowing, because CH_4 and C_2H_6 are oxidized at 200°. In this procedure, the absorption of the hydrogen is really a combustion. Objection to the use of palladium in any form as an absorbent is based on the fact that some water is always likely to be formed when oxygen is present.

(b) Determination by Combustion

Mix a measured volume of the gas with more than half as much oxygen and burn the hydrogen by one of the following methods. The hydrogen can be determined by measuring the contraction in total volume.

$$2H_2 + O_2 = 2H_2O$$
2 vols. 1 vol 0 vol.
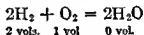
It is evident that, by the combustion of 2 volumes of hydrogen, 3 volumes of gas will disappear (the water formed occupies a negligible volume). The contraction, therefore, is equal to $\frac{3}{2}$ the volume of the hydrogen consumed. If the contraction is denoted by V_C and the volume of the hydrogen by V_H, then $V_C = \frac{3}{2}V_H$, and consequently $V_H = \frac{2}{3}V_C$. Since the molar volumes of hydrogen and oxygen are practically the same, this last statement is true without any correction.

In many cases the weight of the water formed is determined by absorption in weighed calcium chloride tubes; from the gain in weight, p, the volume of hydrogen is computed as follows: $\frac{22,405}{18.016} \times p =$ 1243 $\times p$ ml hydrogen under standard conditions.

Combustion of Hydrogen with Copper Oxide[1]

In the ultimate analysis of organic compounds (cf. p. 354) the hydrogen is almost always determined by passing the vapors over glowing copper oxide. Suitable apparatus has been devised for the application of the same principle to gas analysis. The explosion method (cf. Fig. 107, p. 704) is often used for determining hydrogen and methane, but the most convenient one is the *slow-combustion* method which will be considered after the combustion with copper oxide has been explained.

The Copper Oxide Tube. This tube is made of Pyrex-glass tubing bent into a shape which reminds one of an inverted Gooch crucible funnel (cf. p. 30). The tubing has an outside diameter of 7 mm and an inside diameter of about 4 mm. The entire apparatus is about 18 cm long, 6.25 cm wide at the bottom, and the legs, which are shaped like the stem of a Gooch crucible funnel, start at 4.4 cm from the bottom and are only about 2 mm apart. The vertical legs of this elongated U-shaped tubing is filled, to the first bend in each leg, with fine-wire copper oxide containing particles of metallic copper evenly distributed throughout the charge. The metallic copper acts as a catalyzer, and without it the combustion is too slow, particularly when the tube is first used. Next to the copper oxide mixture, in the nearly horizontal parts of both legs, there is a packing of fine glass wool, but the widely separated vertical legs of the apparatus, which correspond to the sides of the cup of a Gooch funnel, are left empty. The tube is provided with a blower through which compressed air can he led to cool it after each combustion.

An electric heater is provided for heating the copper oxide. The heating element is coiled upon an Alundum core which is insulated from the brass jacket with Silocel or a mixture of sodium silicate, magnesium oxide, and asbestos. A thermometer is provided, and the temperature of the copper oxide must be kept a little under 310° during a combustion. The heating element is placed in series with a rheostat of suitable resistance and amperage so that the furnace can be heated to 300° within 20 minutes and kept at this temperature within 5° for any length of time.

To carry out a combustion, turn on the switch and adjust the rheostat so that, by the time the gas is needed, the temperature will be between 290° and 310°. Then, after the gas has been mixed with a measured volume of oxygen, drive over the mixture into the manifold as far as the first stopcock which leads to the copper oxide tube. Place the heater over the tube and turn the stopcock nearest the buret to connect it with the copper oxide tube. Raise the leveling bottle on the buret and slightly lower the one connected to a so-called *slow-combustion pipet*.

The *slow-combustion pipet* is made of Pyrex glass and has a capacity of 170–180 ml with the stopper inserted. It is provided with an electrically heated coil, and in it the combustion of the gas can take place. In the present case, it is used merely for storage and to effect the transfer of the gas to the copper oxide tube at the proper rate. The pipet can be obtained from dealers in chemical apparatus with full directions regarding its use.

Turn the stopcock above the slow-combustion pipet to connect this vessel with the copper oxide tube, and turn the second stopcock slowly so that the gas enters

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[1] This and the following procedure are adapted from *Methods of the Chemists of the United States Steel Corporation for the Sampling and Analysis of Gases*, published by the Carnegie Steel Company of Pittsburgh, Pa. The booklet is inexpensive and should be in the hands of all chemists engaged in the technical analysis of gases. It contains about 25 illustrations of modern apparatus besides many useful procedures and tables.

the copper oxide tube at the rate of about 15 ml per minute. When the liquid in the buret has reached the tube, lower the leveling bottle of the buret and draw back the gas at the same rate. Draw the gas back and forth several times. Next raise the heater and cool off the copper oxide tube with compressed air. When the tube reaches room temperature, return the gas to the buret and measure the volume. The copper oxide becomes exhausted eventually but can be revivified by heating to 350° and passing air through the tube several times.

Slow-Combustion Method. Transfer a suitable measured volume of oxygen to the slow-combustion pipet under slightly reduced pressure. Turn the dial on the rheostat to the line marked "Start Here" and pull the switch to the place marked "Slow Comb." Now slowly turn the dial on the rheostat in a clockwise direction until the coil is bright yellow in color and adjust the valve on the air line to the blower so that sufficient cold air is blown against the top of the buret to keep the top cool. Then turn the stopcocks so that air slowly enters the pipet. If the content of combustible gas is high, the gas should ignite at once, but if the content is low and mostly hydrogen, the actual combustion may not be noticeable. Gases containing hydrogen will ignite and burn with the coil at a much lower temperature than those from which hydrogen is absent, probably as a result of the catalytic action of platinum on the combustion of hydrogen. When the gas is all out of the buret, adjust the leveling bottle so that the gas returns to the buret and is passed back and forth over the hot coil several times.

9. Methane, CH_4. Mol. Wt. 16.04

Density = 0.5545 (air = 1). Weight of 1 l = 0.7168 g
Molar volume = 22.36 l. Critical temperature = −82°C

ABSORPTION COEFFICIENTS OF METHANE FOR WATER*

Temperature	β	Temperature	β
0°.....	0.05563	30°... .. .	0.02762
5°.. ...	0.04805	35°.. .	0.02546
10°......	0.04177	40°. ..	0.02369
15° .. .	0.03690	45°	0.02238
20°	0.03308	50°.	0.02134
25°...... ..	0.03006	55°....,.... .	0.02038

*L. W. Winkler, *Ber.* **34**, 1419, (1901).

In alcohol, methane is about 10 times as soluble as it is in water.

Inasmuch as no satisfactory absorbent for methane is known, it is always determined by combustion. From the equation representing the combustion, $CH_4 + 2O_2 = CO_2 + 2H_2O$, the following deductions can be made:

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$
$$\text{1 vol} \quad +2 \text{ vols} \quad \text{1 vol.} \quad \text{0 vol.}$$

1. **Contraction.** The contraction caused by the combustion of methane is equal to twice its original volume.

2. **Carbon Dioxide.** By the combustion of methane an equal volume of carbon dioxide is produced.

3. Oxygen Consumed. For the combustion of 1 volume of methane 2 volumes of oxygen is necessary.

In these assumptions, however, it should be borne in mind that the molar volume of $CH_4 = 22.36$ l, that of $O_2 = 22.39$ l, that of $CO_2 = 22.26$ l, and the gas is saturated with moisture. Actually the above equation reads: 22.36 l of methane reacts with 22.39 l of oxygen to form 22.26 l of carbon dioxide which is saturated with moisture. Cf. p. 715.

ANALYSIS OF ILLUMINATING AND PRODUCER GASES

The analysis of all such gases can be accomplished either by the method of Hempel[1] or by that of Drehschmidt.[2]

Hempel's Method

Hempel's apparatus is shown in Fig. 101, p. 679. It consists of a eudiometer, W, with 0.2-ml graduations and connected by means of rubber tubing with the leveling bulb K. The eudiometer is also connected with the compensation tube D, which in turn is connected with

a manometer C; both the tubes W and D are surrounded by a cylinder containing water.

Calibration of the Apparatus. First fill the manometer tube with mercury by raising the leveling bulb K with the stopcock P in the position shown in Fig. 101, so that there is an open connection between W and c. Allow the mercury to pass over into C until the mark mm is reached. Then determine the volume of the manometer tube from the mark m to the point a (Fig. 101) as follows:

By carefully lowering the bulb K draw the mercury over into C exactly to the point a when the stopcock P is closed. Allow a little air to enter into the eudiometer through the right-hand capillary tube above P (the tube E should be withdrawn as in Fig. 108). Place the leveling bulb K upon a solid support so that the mercury level in it is at the same height as in W, and with the stopcock P still open, read the

Fig. 108.

position of the mercury in W. Close the stopcock, raise K a little, and turn P to the position shown in Fig. 101. By raising K still higher,
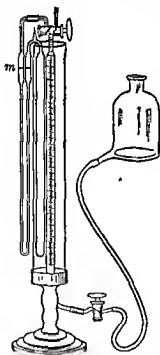
[1] *Gasanalytische Methoden* (1900).

[2] *Ber.,* 21, 3242 (1888).

drive the air over into the manometer tube C until the mercury has exactly reached the mark m, then close the stopcock A (Fig. 101). Then adjust the position of the mercury by turning the stopcock p one way or the other, and once more read the position of the mercury in W. The difference between the two readings represents the volume of the tube between the marks m and a, an amount which must be added to all subsequent readings.

Introduce a drop of water at c, by means of a fine pipet, into the compensation tube D and either fuse together the end of the tube, or close with a cork stopper and make air-tight with sealing wax.

Procedure for the Analysis. If the analysis is to be carried out on the spot, collect a large sample of the gas in a Drehschmidt pipet (Fig. 101 S). To accomplish this, connect the capillary tube E' by means of rubber tubing with the source of the gas, and turn the stopcock M so that the tube E' is in connection with the bulb of the pipet with the leveling bulb and the stopcock s open. Fill the pipet with the gas, then turn the stopcock M so that it communicates with the outer air, and completely expel the gas from the pipet. In this way draw the gas in and out of the pipet at least 3 times to make sure that all foreign gas (air) is removed from the rubber tubing. Then collect the sample of gas and close the two stopcocks M and s.

In order to bring the gas to be tested from the Drehschmidt pipet into the eudiometer, connect the two instruments by means of the capillary E' (imagine the capillary E in Fig. 101, p. 679, to be replaced by E') and firmly wire the rubber connections to the glass. Turn the stopcock M to the position shown in Fig. 101, raise the leveling bulb K (after previously causing the mercury in the manometer tube to reach to the point a) and fill the buret with mercury until it begins to flow from out of the tip of the key at M; then close the cocks A and p. Turn the cock M so that the pipet S and the buret W are in connection, raise K', open s, lower K, and open both p and A.

After about 40 ml of the gas has passed over into the eudiometer, close the cocks A and M, dip the key of the stopcock M (which must be entirely filled with mercury) into a beaker containing mercury, and suck the gas in the capillary into W by lowering K and opening A and p. As soon as the capillary E is entirely filled with mercury, close A, p, and finally M.

Now determine the volume of the gas in W as follows: Open A and raise K so that the mercury in the bulb is a little higher than it is in W. After this open p and drive the gas over towards C until the mercury in both arms of the manometer tube is at about the same height; then close A immediately. Make the last fine adjustment of the mercury

levels within the tubes by closing or opening the screwcock Q. Read the volume of the gas,[1] and to the reading add the correction corresponding to the volume between the marks M and a.

From this point the analysis begins.

1. Determination of Carbon Dioxide

With the stopcock p closed, turn the cock M as shown in Fig. 101, remove the Drehschmidt pipet, and replace by a second, clean pipet completely filled with mercury. On connecting the stopcock M with the rubber connector of the capillary E', it should be in the position shown in the drawing. By this means the mercury in the rubber tubing can flow out through the key. After wiring the rubber tightly to the glass, introduce 3–5 ml of caustic potash solution (1:2) through the key into the pipet M and wash out the alkali in the capillary with about 2 ml of distilled water and then with a little mercury; after this drive over the gas itself into the pipet. When the mercury has filled the whole capillary, both to the right and left of M, close A, p, and M. Raise the bulb K' so that extra pressure is placed upon the gas in the pipet, and close s. Gently shake the pipet for 3 minutes without disconnecting it from the eudiometer, after which return the gas to W as follows: Open M, p, and A; lower K; raise K'; and open s. When almost all the gas has been driven out of the pipet, close M, p, A, and Q; place the leveling bulb on the table below, and K' upon the support (missing from Fig. 101, but shown in Fig. 108) upon which the pipet itself rests. Now open M, p, A, and s, and screw up Q a little so that the gas is very slowly sucked into the buret. As soon as the caustic potash solution has reached M, close it. Now remove the gas remaining in the capillary to the left of M by sucking mercury through the key of M into W. Finally read the volume of the unabsorbed gas in the same way as before. The difference between the two readings represents the volume of CO_2.

2. Determination of the Heavy Hydrocarbons or Illuminants

Remove the pipet containing the caustic potash solution and replace it with another containing fuming sulfuric acid.[2] Drive the gas over

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[1] The reading is best made with the help of a small telescope, the ocular of which is provided with cross hairs. For this purpose the telescope connected with a Bunsen spectroscope is suitable.

[2] In this pipet the bulb tube K' is fused on to the absorption bulb, so that it is a little higher than the latter, in the same way as in the Hempel pipet (Fig. 111). Mercury is acted upon by fuming sulfuric acid.

into the latter, and allow to stand with occasional passes to and fro, for 45 minutes, then empty the pipet in precisely the same way as before. Return the gas to the pipet containing the caustic potash solution in order to remove the acid vapors, and finally transfer to the buret W and read its volume. The difference before and after the treatment with fuming sulfuric acid represents the sum of the heavy hydrocarbons or illuminants (C_2H_4, C_6H_6, C_2H_2, etc.). It is not usually customary to attempt to separate the benzene from the ethylene.

3. Determination of Oxygen

Carry out this part of the analysis in exactly the same way as the determination of the CO_2, but using an alkaline solution of pyrogallol in the absorption pipet (cf. p. 698).

4. Determination of Carbon Monoxide

The determination of carbon monoxide may be effected either by absorption with ammoniacal cuprous chloride or by simultaneous combustion with hydrogen and methane.

For the absorption method, the procedure is the same as in the determination of the heavy hydrocarbons, i.e., the absorption is effected in a pipet containing only ammoniacal cuprous chloride (no mercury). Shake the gas for 3 minutes with a solution of cuprous chloride which has already been used and then the same length of time with a fresh, or little used, solution (cf. p. 703). Before reading the volume of the unabsorbed gas, free it from ammonia vapors, by shaking with $4 N$ hydrochloric acid in a Drehschmidt pipet.

5. Determination of Hydrogen and Methane

After the removal of the carbon monoxide, the gas may consist of hydrogen, methane, and nitrogen. Add an excess of oxygen to this mixture (with illuminating gas twice its volume; with water gas and producer gas only a little more than half as much oxygen is necessary). Connect the eudiometer W with a Drehschmidt pipet entirely filled with pure mercury,[1] using a Drehschmidt platinum capillary (Fig. 101 V, p. 679); heat to bright redness with the non-luminous flame of a Teclu burner, taking care that the inner flame mantle does not come in

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[1] There must be no trace of caustic potash in the pipet because then CO_2 would be absorbed and an inaccurate result would be obtained. To make sure that all the alkali is removed, wash the pipet first with water, then with hydrochloric acid, and finally with water once more.

contact with the platinum. Pass the gas mixture 3 times in a slow stream through the hot platinum tube, but take care that no mercury enters the tube. Then measure the volume of the burned gas without removing the platinum capillary, and determine the carbon dioxide by introducing some caustic potash into the pipet and shaking the gas with it; after 3 minutes' shaking, return the unabsorbed gas to the eudiometer, closing the stopcock M as soon as the caustic potash solution reaches it.

Calculation of Hydrogen and Methane

Assume V ml of gas to be taken for the analysis. The residue remaining after the absorption of the CO_2, C_nH_{2n}, O_2, and CO is mixed with oxygen and burned. The contraction produced is V_c, and the CO_2 formed amounted to V_K.

It was shown on p. 709 that the volume of the methane is equal to the volume of the CO_2 formed, V_K, and in percentage: $\dfrac{V_K}{V} \times 100 =$ per cent CH_4.

Since, by the combustion of 1 volume of CH_4, 2 volumes of gas disappear, it is evident that by the combustion of V_K ml of CH_4 the contraction will amount to $2V_K$.

If the latter value be subtracted from the total contraction V_c, the difference represents the contraction caused by the combustion of the hydrogen present $(V_c - 2V_K)$, and two-thirds of this represents the amount of hydrogen. Therefore $200\dfrac{(V_c - 2V_K)}{3V} =$ per cent H.

Slight errors are introduced unless the differences in molar volumes are considered and the fact that the gas is moist from the water formed (cf. p. 686).

Determination of Carbon Monoxide, Methane, and Hydrogen by Combustion

After the absorption of the CO_2, C_nH_{2n}, and O_2, the residual gas consists of CO, CH_4, H_2, and N_2. Add a measured volume of oxygen,[1] explode the mixture, and determine both the contraction, V_c, and the

[1] The purity of the oxygen must be tested before the analysis, because the commercial product almost always contains nitrogen. To a measured volume of nitrogen add a definite amount of oxygen, as otherwise the amount of the residual gas might be too small to fill the manometer tube between the marks a and m (Fig. 101). Prepare the nitrogen by allowing air to stand over phosphorus in a Hempel pipet. (Cf. p. 698.)

carbon dioxide formed, V_K. After this determine the unused oxygen by absorption with alkaline pyrogallol solution. If the excess of oxygen is subtracted from the amount originally added, the difference will give the amount of oxygen necessary for the combustion, V_O.

If the volume of CO is denoted by x, the CH_4 by y, and finally the H_2 by z, the following three independent equations hold true:

1. $V_C = \frac{1}{2}x + 2y + \frac{3}{2}z$

2. $V_K = x + y$

3. $V_O = \frac{1}{2}x + 2y + \frac{1}{2}z$

and from these equations

$$x = \frac{2}{3}V_K + \frac{1}{3}V_C - V_O = CO[1]$$

$$y = V_O = \frac{1}{3}(V_K + V_C) = CH_4$$

$$z = V_C - V_O = H_2$$

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[1] According to A. Wohl (*Ber.*, 1904, 433) the results are not quite accurate when obtained in this way because the molar volume does not always equal the assumed value of 22.41 l Nernst, in his book, *Theoretical Chemistry*, gives the following molar volumes:

For 1 g mole of the gas,	or referred to oxygen
$H_2 = 22.43$ l	$H_2 = 1.0017$
$O_2 = 22.39$ l	$O_2 = 1.0000$
$CO = 22.39$ l	$CO = 1.0000$
$CH_4 = 22.44$ l	$CH_4 = 1.0020$
$CO_2 = 22.26$ l	$CO_2 = 0.9939$

Taking these values into consideration, A. Wohl obtains for xCO, yCH_4, and zH_2, the following formulas:

$$x = 0.3329V_C - V_O + 1.3394V_K$$
$$y = -0.3336V_C + 1.0020V_O - 0.3340V_K$$
$$z = 1.0005V_C - 1.0017V_O - 0.0060V_K$$

F. Haber (*Thermodynamik techn Gasreaktionen*) sees no reason for modifying the Bunsen formulas in this way, for, when a combustion analysis is carried out by explosion, the volume of gas after the explosion is so poor in carbon dioxide that the partial pressure of the latter does not vary much from that of an ideal gas and, therefore, follows Avogadro's rule.

It is quite another matter with mixtures rich in carbon dioxide, as often occur in gas-volumetric analyses. In such mixtures the weight of carbon dioxide (or of carbonate) is computed from the volume of the gas and accurate values are obtained by using the actual molar volume of 22.26 for this gas (see p. 330).

The necessity of using the actual molar volume instead of the theoretical value has been shown by Treadwell and Christie (*Z. angew Chem.*, 1905, 1930) for chlorine. With other vapors (NH₃, HCl, SO₂, N₂O) the observed molar volume should also be used.

Analysis according to H. Drehschmidt[1]

The apparatus of Drehschmidt, like that of Hempel, consists of the gas buret B and the compensation tube C, both of which are contained in a cylinder filled with water (Fig. 109).

Through the stopcocks a and b, connect B and C, by means of capillary glass tubing containing a drop of a colored solution (indigo and
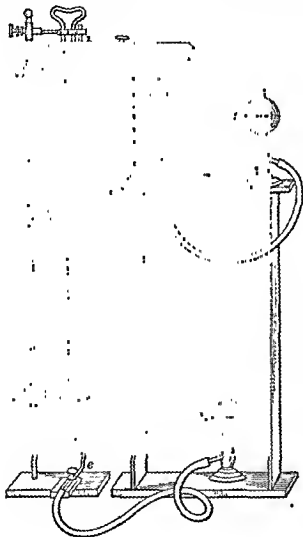
Fig. 109.

sulfuric acid); in order to determine the position of the solution, the capillary is provided with a millimeter graduation. The three-way cock a can be turned so that C connects with the outer air or with the capillary, or so that the capillary is in connection with the air; it has an opening through the top of the key. The cock b has a right-angled boring like

[1] Ber., 21 3242, (1888).

H, Fig. 101. The buret is divided into millimeters and must be calibrated with mercury before using. The apparatus is used in the same way as described under the Hempel method, p. 710.

TECHNICAL GAS ANALYSIS

Method of Hempel

The apparatus necessary is shown in Fig. 110. It consists of a long measuring tube ending at the top in a thick-walled capillary tube and connected at the bottom by means of rubber tubing about a meter long with the leveling tube.

The gas is confined over water which has been saturated with the gas to be examined, and the absorption is effected in Hempel's absorption pipets such as are shown in Figs. 111, 112, 113, and 114. Figure 111 represents a *simple* pipet for liquid absorbents, and Fig. 112 shows a *compound* absorption pipet. This is used for solutions which undergo change on exposure to the air, e.g., an alkaline solution of pyrogallol, or an ammoniacal cuprous chloride solution. The liquid in the two right-hand bulbs serves to protect the solutions on the left. Figure 113 shows the pipet used for fuming sulfuric acid. The small bulb is filled by the
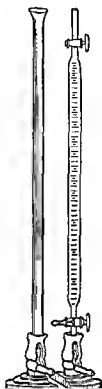
Fig. 110.
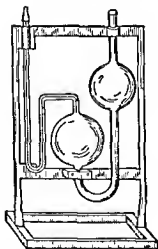
Fig. 111.
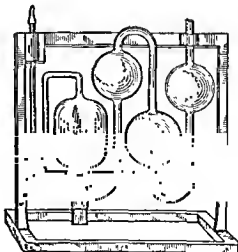
Fig. 112.

glass blower with glass beads, which serve to give to the sulfuric acid the largest possible surface, so that the absorption is effected much more readily. Figure 114 is a pipet used for solid absorbents, such

as phosphorus. In order to fill it with phosphorus, hold the pipet upside down, fill the cylindrical part with distilled water, and introduce small sticks of colorless phosphorus. After filling the pipet, insert the
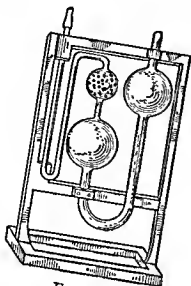
Fig. 113.
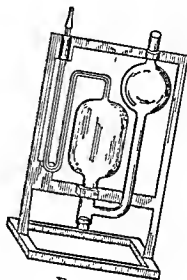
Fig. 114.

rubber stopper, place the apparatus right side up, pour water into the bulb, and remove any air bubbles in the cylindrical part of the pipet by blowing through the bulb until the water flows out from the top of the left-hand capillary; then close by means of rubber tubing and a pinch-cock.

Analysis of Illuminating Gas

First, prepare the confining liquid by conducting the gas through distilled water in a wash bottle for several minutes with constant shaking. Completely fill the gas buret with this liquid and then close the upper rubber tubing with a pinchcock. To fill the buret with gas, connect the receiver with the buret by a piece of rubber tubing through which the gas has been flowing for 2 or 3 minutes, lower the leveling tube, open the pinchcock, and allow a little more than 100 ml of the gas to flow into the buret. Now close the upper cock, raise the leveling tube until the lower meniscus of the confining liquid is exactly at the 100-ml mark, then close the rubber between the leveling tube and the buret with a pinchcock placed near the buret, and allow the apparatus to stand until the water no longer rises in the buret; this requires 2–3 minutes. When the water is stationary, carefully open the lower pinchcock (for there is excess pressure in the buret) which causes the water level to sink. When the 100-ml mark is again reached, close this cock, and open the upper pinchcock an instant to allow the excess

of gas to escape and then immediately close. To make sure that the buret contains exactly 100 ml of the gas, open the lower pinchcock, and after bringing the water in the leveling tube to the same height as in the buret, take the reading; the lowest point of the meniscus should coincide exactly with the 100-ml mark of the buret. Finally close the lower pinchcock.

1. Determination of Carbon Dioxide

Connect the buret with a pipet such as is shown in Fig. 111 containing caustic potash solution, by means of a capillary filled with water, raise the leveling tube, open first the lower pinchcock and then the upper one,[1] and drive the gas over into the pipet. The confining liquid should now fill the entire capillary. Close the upper pinchcock and shake the pipet and its contents for 3 minutes.[2] Return the gas to the buret, taking care that none of the alkali enters with it.

Bring the liquid in the leveling tube to the same level as that in the buret; close the lower pinchcock, and after the water has completely drained from the sides of the tube, read the volume of the unabsorbed gas.

2. Determination of the Heavy Hydrocarbons, or Illuminants, C_nH_{2n}

Connect the buret by a dry, empty capillary with sulfuric acid pipet (Fig. 112) and pass the gas back and forth 4 times, taking care that no water enters the pipet and that the sulfuric acid does not reach the rubber connection.

Before the experiment mark the position of the sulfuric acid upon the milk-glass plate back of the pipet; at the end of the experiment the acid must come to the same mark. The gas in the buret is now contaminated with acid vapors which are removed by passing it into the potash pipet, afterwards returning it to the buret.

3. Determination of Oxygen

This can be effected by shaking the gas in the compound pipet with alkaline pyrogallol solution, but far preferably by means of phosphorus. In the latter case, drive the gas over into the phosphorus pipet and

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[1] In the figure this pinchcock is lacking.

[2] The absorption takes place more rapidly with one of Hempel's newer pipets, which are similar to the one shown in Fig. 112, except that the right-hand bulb is replaced by a movable leveling bulb, as in Fig. 101. The latter is filled with mercury, upon which the liquid absorbent floats. For the absorption of CO_2, it is necessary to pass the gas back and forth only once

allow it to remain there until the white vapors disappear; this usually requires but 3–4 minutes (cf. p. 698). If no white vapors can be detected, this shows conclusively that the absorption of the heavy hydrocarbons was incomplete (cf. p. 699). In such a case, the gas must be again treated with sulfuric acid and afterwards with phosphorus. If no white fumes are then formed, no oxygen is present, a condition which practically never occurs, for in the determination of the hydrocarbons a little air containing oxygen always reaches the gas from the small capillary.

4. Determination of Carbon Monoxide

Shake the gas 3 minutes with an old solution of ammoniacal cuprous chloride and then the same length of time with a fresh solution. (See pp. 703, 713.)

5. Determination of Hydrogen and Methane

After the absorption of the carbon monoxide place the residual gas in the hydrochloric acid pipet and wash the buret with hydrochloric acid to remove traces of alkali, and then fill with distilled water.

(a) Transfer 15–16 ml of the gas in the hydrochloric acid pipet to the buret, and, after reading its volume, drive it over into an explosion pipet containing mercury (Fig. 107, p. 704). Accurately measure 100 ml of air (containing 20.9 ml of oxygen) in the buret and add to the contents of the explosion pipet. Then close the pipet by a pinchcock, mix the contents of the pipet by shaking, lower the leveling tube so that the gas is placed under reduced pressure, and close the glass stopcock of the pipet. Connect the platinum wires, which are fused in the upper part of the bulb, with the poles of a small induction coil so that sparks pass between the platinum points within the pipet. The explosion at once occurs with a flash without breaking the pipet. Return the gas to the buret. Objection has been raised to reading the volume of the gas and then determining the amount of carbon dioxide formed, as a measure of the amount of methane burned, because the gas in the buret is confined over water which absorbs appreciable quantities of carbon dioxide. It has been found, however, that the error caused by absorption of CO_2 by the water is so slight, during the short time of waiting, that it is best to determine the CO_2 with caustic potash after the explosion, as Hempel also recommended. (See p. 721.) Finally, determine the amount of unused oxygen by means of absorption with phosphorus. If the excess of oxygen is subtracted from the total volume added (20.9 ml), the amount of oxygen required for the combustion is

known (V_0), so that we have two equations from which the amount of hydrogen and methane can be computed.

If x is the volume of the hydrogen and y the volume of the methane, we have

$$(1) \ V_C = \tfrac{3}{2}x + 3y \qquad (2) \ V_O = \tfrac{1}{2}x + 2y$$

and

$$x = \tfrac{4}{3}V_C - 2V_O \qquad y = V_O - \tfrac{1}{3}V_C$$

The values thus obtained are referred to the total gas residue, and in this way the amount of hydrogen and methane present in the illuminating gas can be determined.

Great accuracy is naturally not to be expected by such an analysis, but the procedure is very satisfactory for an approximate estimation.

Better results are obtained by the

(b) *Method of Winkler-Dennis.* In this method, the entire gas residue is transferred to a Hempel pipet (Fig. 115) containing mercury and connected with a leveling bulb. Through the rubber stopper at the bottom two steel needles are inserted (knitting needles), the longer of which is enveloped throughout its whole length by a glass tube, and the upper end is connected, at about three-quarters the height of the cylindrical part of the pipet, with a thin platinum spiral.
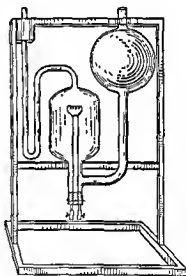
FIG. 115.

Connect the pipet with a Hempel buret containing 100 ml of oxygen over water, produce a lower pressure in the oxygen buret by lowering the leveling tube and then closing the rubber tubing with a screwcock; after this place the leveling tube in a high position. Now connect the bottom ends of the two needles of the pipet with the wires of a small storage battery of such a strength that the platinum spiral is heated to dull redness. By lowering the leveling bulb, reduce the pressure in the pipet slightly, and by opening the two upper screwcocks between the pipet and the oxygen buret and gradually opening the lower screwcock on the buret conduct a very slow stream of oxygen into the pipet. Since a large excess of the gas residue is present at the start, the combustion takes place quietly; explosions never occur. During the combustion the platinum spiral begins to glow more brightly; to prevent its melting, place a variable resistance in the circuit to regulate the strength of current and the glowing of the platinum.

As soon as all the oxygen is in the pipet, allow the spiral to glow 2–3 minutes longer, then stop the electric current and allow the gas to remain in the pipet for 15 minutes so that it will assume the room temperature. Then transfer to a Hempel buret and measure its volume. Determine the carbon dioxide in the usual manner.

Remark. The Winkler-Dennis pipet is open to the objection that the rubber stopper eventually leaks; for this reason the form of apparatus devised by M. Bretschger, as shown in Fig 116, is preferable.

The gas residue instead of being burned according to the Winkler-Dennis method, may be conducted over glowing cupric oxide (cf. p. 708).
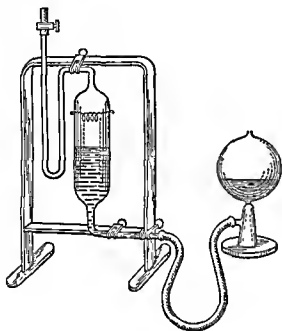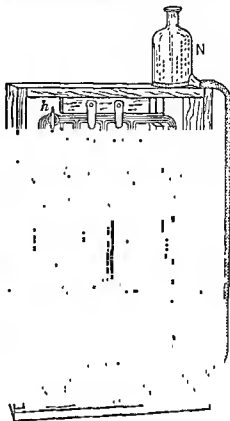
FIG. 116.   FIG. 117.

Orsat's Apparatus

For the analysis of flue gases, Orsat has constructed the apparatus shown in Fig. 117. It consists of the 100-ml measuring tube B surrounded by a cylinder containing water, and connected on the one hand with three Orsat tubes by means of the cocks, I, II, III, and on the other hand with the outer air through the stopcock h. The Orsat tube III contains caustic potash solution, II alkaline pyrogallol solution, and I ammoniacal cuprous chloride solution.

Manipulation. By raising the leveling bottle N and opening the stopcock h, fill the measuring tube B with water. As soon as the water is above the mark in the widened part of the measuring tube,

close the rubber tubing between the leveling bottle and the measuring tube by a pinchcock. Connect a with the source of the gas; draw it into the measuring tube by lowering the leveling bottle and opening the pinchcock. The U-tube on the left side of the apparatus is filled with glass wool and serves as a filter; any smoke being removed from the gas to be examined. The sample thus collected is naturally contaminated with the air from the rubber tubing, the U-tube, and the capillary, which must be removed. The cock h serves for this purpose and is provided with a T-boring. Turn the cock so that the buret communicates with the outer air through a small tube (not shown in the illustration), and expel the gas by raising the bottle N. Repeat this process of filling and emptying 3 times, and use the fourth filling of the tube B for the analysis. Bring the gas in the buret to the zero mark, and place it under atmospheric pressure by quickly opening and then closing h. After this drive over the gas into the potash bulb and back again to the measuring tube several times, until there is no further absorption; after this again read the volume of the gas. In the same way pass the gas successively into the pyrogallol and the cuprous chloride tubes, thus obtaining the volumes of CO_2, O_2, and CO in the gas.

The chemists of the United States Steel Corporation analyze various gas mixtures daily. Blast-furnace gas, coke-oven gas, producer gas, natural gas, and flue gas are analyzed regularly, and the chemists are frequently called upon to analyze sewer gas, mine air, water gas, exhaust gas, compressed fuel gas, compressed oxygen, compressed nitrogen, nitrogen and hydrogen mixtures, etc. They have devised an apparatus of the Orsat type which has proved satisfactory for the examination of all these gases in the laboratory They also use a portable Orsat apparatus which is very similar to that shown in Fig. 117 The larger laboratory apparatus has many distinct improvements It has, for example, three different bulbs for leveling and flushing, an air compressor, resistance coils for heating the gases, and a slow-combustion pipet. In designing the apparatus, the attempt was made to avoid error due to inaccuracy of the buret graduations and errors caused by the capillary space that may be left when the gas mixture is transferred to the gas buret for measurement The burets used with this apparatus have a capacity of 100 ml, and the graduations extend for a distance of about 67 cm from the top shoulder which makes the straight fuel gas buret easily readable to within 0 05 ml. When the gas is confined over water, the Shellbach buret is recommended as convenient in reading. The error due to unused capillary space has been practically eliminated The stopcocks are of special design and, as usual, are placed at the top in the main line of manifold which is made of capillary tubing arranged so that liquid from each of the twelve pipets can be drawn up to its own stopcock and all the gas in the manifold can be driven over into the buret by means of water or an aqueous solution from a flushing pipet Thus the entire capillary space is left filled with water after each determination so that the capillary error is eliminated and no preliminary flushings are required to prepare the apparatus for use The buret is encased in a glass mantle of about twice the diameter of the buret It is kept filled with water, and errors due to slight temperature changes, which affect both the volume of the gas and the water

content, are practically eliminated during the 45 minutes or so while the gas is being analyzed in a laboratory of which the temperature is under thermostatic control. A compensating device is provided (cf. p. 331) so that all buret readings are made under a pressure which is independent of the atmosphere.

Two burets are used with this apparatus, one for flue gas, fuel gas, etc., and the other for mine air and other mixtures containing very small quantities of some important constituents. A manometer is attached to the buret. It is made of capillary tubing and is of an improved design. An automatic leveling bulb is also provided.

At the steel plants, *flue gases* are tested in one of three ways: (1) The carbon dioxide, oxygen, and carbon monoxide are determined separately by absorption; the hydrogen and methane are determined by explosion. The residual gas, after the excess oxygen has been absorbed, is assumed to be nitrogen. (2) The carbon dioxide, oxygen, and carbon are determined by absorption, and the hydrogen and methane by slow combustion. (3) The carbon dioxide, and the hydrogen and oxide, and other combustibles by slow combustion.

Blast-furnace gas is analyzed for carbon dioxide, oxygen, and carbon monoxide by absorption and other combustibles by explosion or slow combustion. Sometimes, after the first three absorptions, hydrogen is determined in the copper oxide tube and hydrocarbons by slow combustion. A third procedure is used in which only the first two absorptions are made at the start, then carbon monoxide and hydrogen are determined with the copper oxide tube and hydrocarbons by slow combustion. A fourth procedure calls for separate absorption of carbon dioxide and oxygen, followed by explosion with a known volume of oxygen and determination of the unused oxygen.

Coke-oven and bench gases are analyzed like producer gas (p. 717) except that a separate test is conducted for hydrogen sulfide (cf. p. 620) and a correction is made for its presence.

Natural Gas. A qualitative test for hydrogen sulfide is made; if bydrogen sulfide is found it is determined by titration (cf. p. 620). With this gas it is necessary to make sure that all absorbent solutions are saturated with the gas. Carbon dioxide is determined as usual by absorption with alkali hydroxide solution. Oxygen is then determined by absorption with chromous chloride, which is preferred to alkaline pyrogallate solution because the latter absorbs some of the hydrocarbons. If the contraction after treatment with chromous chloride is over 0.2 ml, it is assumed to represent oxygen and is calculated as such. Sometimes, however, the titration method (p. 701) is used for determining oxygen. After the oxygen absorption with chromous chloride, carbon monoxide and unsaturated hydrocarbons are determined by passing the gas through the cuprous sulfate and β-napbthol reagent (cf. p. 703). Finally the paraffins are determined by mixing with oxygen, burning in the slow-combustion pipet, measuring the contraction, and then absorbing the CO₂ formed. From these data, methane and ethane are calculated on the assumption that they are the only paraffins present, which is not quite true.

Mine air is tested for carbon dioxide (by absorption in alkali hydroxide solution), oxygen (by means of chromous chloride), and carbon monoxide (with cuprous sulfate and β-napbthol reagent). A special detector can be purchased which will indicate the presence of less than 0.01 per cent of carbon monoxide.

Bunte's Apparatus

This apparatus, shown in Fig. 118, differs from those previously described, inasmuch as the absorption takes place in the measuring vessel itself, whereas in the others it takes place in the pipets.

The Bunte buret has a capacity of 110–115 ml between a and b; a is a three-way cock, while b is bored only once.

Manipulation. Connect the buret with the leveling bottle N as shown in the illustration, open a and b, and allow the water to run up to the mark in the funnel above a. Connect the key of the stopcock a with the source of the gas, lower N, turn a to the proper position, and draw the gas into the buret. After 101–103 ml of the gas has entered the buret, close a and b, raise N, and by opening b compress the gas in the buret until the confining liquid has exactly reached the zero mark. Now cautiously open the cock a, when some of the gas in the buret will escape through the water in the funnel. The gas in the buret is now under a pressure equal to that of the atmosphere plus the pressure from the column of water in the funnel, and all subsequent measurements are taken under the same conditions.

Absorptions. In order to introduce the different absorbents into the buret connect its lower end by means of the rubber tubing h with the bottle F containing a little water and with the water blown up into the rubber tubing. Open the cock b and the screwcock h. Allow the water in the buret to run out until it exactly reaches the cock b, which is then closed. Place the absorbent in a small dish, introduce the lower tip of the buret into the liquid, and open the cock b. Inasmuch as the gas in the buret is under less than atmospheric pressure, the absorbent is sucked up into the buret. Now close the cock b, grasp the buret above a and below b (in order not to warm the gas), and shake its contents well; again dip the tip of the buret into the absorbent in the dish and draw up a little more of the absorbent into the buret. Repeat this process until no more of the absorbent is sucked up into the buret. It would now be incorrect to read the volume of the unabsorbed gas, for it is under a pressure quite different from that at the beginning of the analysis, namely, the atmospheric pressure less the pressure of the column of liquid remaining in the buret with the cock b open. Further-
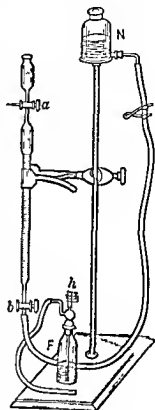
Fig. 118.

more the vapor tension of the liquid in the buret is different from that of the water originally present. In order to obtain the original conditions, connect the buret with the bottle F, which now contains only enough water to fill the rubber tubing and the glass tube, and drain off the absorbent from the buret into the bottle until the upper level of the liquid reaches the cock b.[1] Then dip the end of the buret into a dish containing water, which rises into the buret on opening b. Close the latter and allow water to run into the buret from the funnel until the original pressure is established, when the volume of the gas is once more read. The difference gives at once the percentage of absorbed gas.

By means of this excellent method the carbon dioxide can be removed by caustic potash, heavy hydrocarbons by bromine water, oxygen by alkaline pyrogallol solution, and carbon monoxide by cuprous chloride.

ANALYSIS OF GASES WHICH ARE ABSORBED CONSIDERABLY BY WATER

Under this heading belong N_2O, SO_2, H_2S, Cl_2, SiF_4, HF, NH_3, etc.

1. Nitrous Oxide, N_2O.   Mol. Wt. 44.02

Density = 1.5297 (air = 1).[2]   Weight of 1 l = 1.9766 g
Molar volume = 22.261.   Critical temperature = $+36°C$

The determination of nitrous oxide can be effected with accuracy by combustion, and this may be carried out in two different ways:

1. According to Bunsen, by exploding with hydrogen, or according to v. Knorre, by means of the Drehschmidt capillary. The contraction produced is equal to the original volume of the nitrous oxide:

$$N_2O + H_2 = H_2O + N_2$$
$$\text{1 vol.} \quad \text{1 vol.} \quad \text{0 vol.} \quad \text{1 vol.}$$
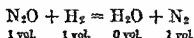
2. According to Pollak, by combustion with pure carbon monoxide, either by explosion or with the help of the Drehschmidt capillary; the volume of the CO_2 formed, which is measured, is equal to the volume of the nitrous oxide:

$$N_2O + CO = CO_2 + N_2$$
$$\text{1 vol.} \quad \text{1 vol.} \quad \text{1 vol.} \quad \text{1 vol.}$$
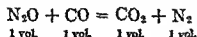
There is no contraction in this case.

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[1] The absorbent is now by no means exhausted; it can be returned to the proper bottle and used for several more determinations.

[2] Lord Rayleigh, *Proc. Roy. Soc.*, **74**, 181 (1904).

2. Nitric Oxide, NO.   Mol. Wt. 30.01

Density = 1.0366 (air = 1).[1]   Weight of 1 l = 1.3402 g
Molar volume = 22 39 l.   Critical temperature = −94°C

ABSORPTION COEFFICIENTS OF NITRIC OXIDE FOR WATER[*]

Temperature	β	Temperature	β
0°..... ..	0.07331	30°. .. .	0.04004
5°...... .	0.06461	35°.....	0.03734
10°.........	0.05709	40°..	0.03507
15°.........	0.05147	45°.	0.03311
20°.........	0.04706	50°..	0.03152
25°.........	0 04323	55°...	0.03040

[*] L. W. Winkler, *Ber.*, **34**, 1414 (1901).

Although nitric oxide is only slightly soluble in water, its determination will be discussed at this place because this gas frequently occurs with nitrous oxide, and must therefore be determined at the same time.

Nitric oxide may be determined by absorption with a concentrated solution of ferrous sulfate or an acid solution of potassium permanganate, likewise, according to E. Divers,[2] by an alkaline solution of sodium sulfate (40 g Na_2SO_3 + 4 g KOH in 200 ml H_2O) with the formation of $Na_2N_2O_2SO_3$.[3] It can be determined accurately, according to Baudisch,[4] as follows: Introduce a measured volume of nitric oxide into an absorption pipet filled with mercury and containing a moist stick of solid potassium hydroxide, and add, from a buret, a measured volume of air. The NO gas is immediately oxidized to N_2O_3, which is absorbed by the potassium hydroxide: $4NO + O_2 + 4KOH = 2H_2O + 4KNO_2$. Since 5 volumes of gas disappear for each 4 volumes of NO originally present, it is evident that the contraction, V_c, is $\frac{5}{4}$ as large as the original volume of NO, and NO = $0.8V_c$.

According to v. Knorre and Arndt,[5] NO can also be determined by combustion. Mix the gas with hydrogen and pass the mixture very slowly through a Drehschmidt capillary (p. 679) heated to bright redness. Under these conditions the nitric oxide is reduced to nitrogen.

$$2NO + 2H_2 = 2H_2O + N_2, \text{ and the volume of NO} = \frac{2}{3}V_c$$

[1] Computed from observations of Gray (1905), Guye and Davila (1906).

[2] *J. Coll. Sci. Imp. Univ. Tokyo*, **11**, 11 (1893).

[3] Nitric oxide is only partially absorbed by an alkaline solution of pyrogallol, forming alkali nitrite, N_2O, and N_2.   C. Oppenheim, *Ber.*, **36**, 1744 (1903).

[4] *Ber.*, **46**, 3232 (1913).

[5] *Ber.*, **21**, 2136 (1889).

If the mixture is passed too rapidly through the capillary tube containing the glowing platinum or if the catalyst is not hot enough, appreciable quantities of ammonia are formed and the results are inaccurate.

It is not possible to carry out the reaction in an explosion pipet: with pure NO and H_2 there is no explosion, and if considerable NO_2 is present the reaction is not quantitative although a very violent explosion may occur.

Combustion of Nitric Oxide and Carbon Monoxide in a Drehschmidt Capillary

According to Henry a mixture of carbon monoxide and nitric oxide is not explosive. On the other hand, according to Pollak, by conducting a mixture of these gases through a Drehschmidt platinum capillary heated to bright redness, the combustion is quantitative if at the same time the carbon dioxide formed is removed by means of caustic potash;[1] otherwise the oxidation is not quantitative. According to the equation

$$\underset{\text{2 vols}}{2NO} + \underset{\text{2 vols}}{2CO} = \underset{\text{0 vol.}}{2CO_2} + \underset{\text{1 vol.}}{N_2}$$
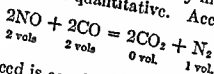
the contraction produced is equal to $\frac{3}{2}$ the volume of the nitric oxide.

Remark. If considerable nitrous oxide is present nt the same time, the combustion in the Drehschmidt capillary takes place quantitatively without the removal of the carbon dioxide. In this case the contraction is half the volume of the nitric oxide.

Analysis of a Mixture of Nitrous and Nitric Oxides

(a) Combustion with Hydrogen

Mix the gas with nn excess of hydrogen and pass it through the Drehschmidt platinum capillary heated to bright redness ns described above. If the volume of the $N_2O = x$ and that of the $NO = y$, we have: (1) $x + y = V$. (2) $x + \frac{3}{2}y = V_c$ (contraction), from which can be calculated: $x = 3V - 2V_c$, $y = 2(V_c - V)$.

(b) Combustion with Carbon Monoxide

To the gas mixture add nn excess of carbon monoxide, pass throcgh the red-hot platinum capillary, and determine first the contraction, V_c, and then the carbon dioxide, V_K. If x is the volume of N_2O, y the

[1] Cover the mercury in the Drehschmidt tube with a concentrated caustic potash solution, by which means the CO_2 is absorbed immediately after its formation.

volume of NO, then $x + y = V_K$ and $\frac{1}{2}y = V_C$, from which it follows that $x = V_K - 2V_C$ and $y = 2V_C$.

Determination of Nitrous Oxide, Nitric Oxide, and Nitrogen in the Presence of One Another

(a) By Combustion with Hydrogen in a Drehschmidt Capillary

After noting the contraction formed by the combustion with hydrogen, add an excess of oxygen to the gas residue and burn the mixture in the Drehschmidt capillary; two-thirds of the contraction which now takes place is equal to the amount of unused hydrogen in the first oxidation. If this quantity is deducted from the amount of hydrogen originally added, the difference, V_H, represents the amount of hydrogen necessary.

We have now:

$$N_2O \quad NO \quad N_2$$
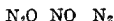
$$1.\ x + \quad y + z = V$$

$$2.\ x + \tfrac{3}{2}y \quad\ = V_C$$

$$3.\ x + \quad y \quad\ = V_H$$

from which we can compute

$$x = 3V_H - 2V_C$$

$$y = 2(V_C - V_H)$$

$$z = V - V_H$$

(b) By Combustion with Carbon Monoxide in the Drehschmidt Capillary

In this case, using the same notation, $x + y + z = V$, $0.5y = V_C$, and $x + y = V_K$ (volume of carbon dioxide). From this it follows that: $x = V_K - 2V_C$, $y = 2V_C$, and $z = V - V_K$.

Determination of Nitrous Oxide, Nitric Oxide, and Nitrogen in the Presence of Carbon Dioxide

The accurate determination of nitrous oxide in the presence of carbon dioxide offers great difficulties. It is not possible to determine nitrous oxide by combustion with hydrogen in the Drehschmidt capillary, because when the carbon dioxide is present it takes part to some extent in the combustion, $CO_2 + H_2 = H_2O + CO$; and the previous absorption of the carbon dioxide by means of a large quantity of caustic potash is equally unsatisfactory, because considerable nitrous oxide

will be absorbed by the reagent. The best way to effect this determination consists in absorbing the carbon dioxide by solid, moist potassium hydroxide contained in an absorption pipet filled with mercury. The difference in volume before and after the absorption gives the volume of CO_2. Transfer the residual gas to the mercury pipet, add a measured volume of air, and absorb the NO as described on p. 727. In the residue determine N_2O according to p. 726, and the N_2 by difference.

3. Nitrogen, N_2. Mol. Wt. 28.02

Density = 0.96727 (air = 1). Weight of 1 l = 1.2505 g
Molar volume = 22.41 l. Critical temperature = −149°C

ABSORPTION COEFFICIENTS OF NITROGEN FOR WATER*

Temperature	β	Temperature	β
0°	0.02348	30°	0.01340
5°	0.02081	35°	0.01254
10°	0.01857	40°	0 01183
15°	0.01682	45°	0.01129
20°	0.01542	50°	0.01087
25°	0.01432	55°	0.01051

* L. Winkler, *Ber.*, **24**, 3606 (1891).

Nitrogen cannot be determined by any of the ordinary methods of gas analysis. It is usually estimated by determining all the other constituents present in a mixture and subtracting the sum of the percentages found from 100.

Technical preparations of nitrogen, prepared from the air, always consist of nitrogen and small amounts of rarer elements. According to Cavendish these latter may be obtained by adding oxygen and allowing a strong electric spark to pass through the mixture. In this way the nitrogen is completely oxidized to nitric acid, which can be removed by means of caustic potash solution. Then, by absorbing the oxygen, the rarer gases are obtained. A still better process is that of Hempel, in which the nitrogen is absorbed by passing the gas over a glowing mixture of 1 g magnesium, 5 g freshly burnt lime, and 0.25 g sodium. The rare gases are not absorbed by this treatment.

According to Bunsen, there is no combustion of nitrogen when detonating gas explodes in the presence of air, provided that not more than 30 volumes of combustible gas are present for each 100 volumes of non-combustible gas. There is no oxidation of nitrogen during a com-

bustion of a gas mixture which is passed through a Drehschmidt platinum capillary.

ANALYSIS OF GASES BY TITRATION OF THE ABSORBED CONSTITUENTS

If a mixture of gases contains several constituents, of which two are removed by the same absorbent, and one of these can be determined by titration, it is a matter of no difficulty to determine the amount of each. The diminution in volume after treatment with the absorbent represents the amount of the two constituents, the titration value represents the amount of one of them, and the difference shows the amount of the other. Such problems can be solved in a variety of ways, and only a few examples will be mentioned.

1. Chlorine, Cl_2. Mol. Wt. = 70.91

Density = 2 488 (air = 1).[1] Weight of 1 l = 3.216 g
Molar volume = 22.04 l. Critical temperature = $+146°$

Determination of Carbon Dioxide in Electrolytic Chlorine[2]

The apparatus shown in Fig. 119 is suitable for this purpose.

Fill the absolutely dry eudiometer, B (the capacity of which between the two stopcocks is accurately known, and for convenience may be 100 ml), through the lower cock, after drying the gas by passing it through a long calcium chloride tube.[3] After 5–10 minutes it is safe to assume that the air has been completely replaced by the gas. Now close the lower three-way cock and then the upper one. Note the temperature and barometric pressure.

Connect the tip of the buret with the reservoir N by rubber tubing. Turn the three-way cock so that the reservoir communicates with the outer air, and then thoroughly wash the lower tip of the buret and the stopcock, and close the latter. Prepare a solution of potassium arsenite by dissolving 4.95 g As_2O_3 in dilute potassium hydroxide, adding dilute sulfuric acid until the solution is neutral to phenolphthalein, and then diluting to 1 l.[4] Place 100 ml of this solution in N and expel any air in

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[1] Leduc, *Compt. rend.*, **116**, 968 (1893); Treadwell and Christie, *Z. angew. Chem.*, **47**, 446 (1905).

[2] Treadwell and Christie, *Z. angew. Chem.*, **47**, 1930 (1905).

[3] If the buret and gas are not perfectly dry, some chlorine will be absorbed by the water. This will not affect the gas reading, but will be harmful in the subsequent titration.

[4] An ordinary solution of arsenite prepared with sodium bicarbonate cannot be used here

the rubber tubing by pinching it with the thumb and finger. By raising N and opening the stopcock, cause a little of the arsenite solution to flow into the buret, which is inclined from side to side in such a way that the walls are thoroughly wet with the arsenite solution. The chlorine is slowly absorbed, as is evident from the fact that the solution slowly rises in the buret. As soon as there is no further absorption, close the lower stopcock and make the solution in the buret flow back and forth several times, by inverting the buret and then turning it back again. After 1–2 minutes all the chlorine will have been absorbed. Then in order to absorb all the carbon dioxide present, lower the tube N, pour 10 ml of potassium hydroxide solution (1 : 1) in the funnel, and carefully introduce it into the buret. Again close the stopcock and run the alkali solution back and forth in the buret.
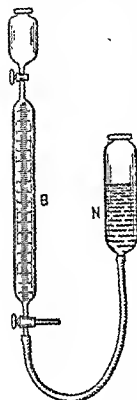
After bringing the liquid in the buret and in the leveling tube to the same height, take the reading. By deducting this from the original volume of the gas, the volume of the chlorine plus that of the carbon dioxide is obtained. To determine the chlorine, empty the contents of the buret and of the leveling tube into a large Erlenmeyer flask and turn the stopcock to the position shown in the drawing so that the liquid in the rubber tubing can flow out. Remove the tubing from the buret and rinse it out with distilled water which is also allowed to run into N. Now add the contents of the buret and rinse the buret itself with distilled water.

Fig. 119.

To the contents of the Erlenmeyer flask add 2 drops of phenolphthalein solution, hydrochloric acid until the red color just disappears, 60 ml of 3.5 per cent sodium bicarbonate solution, and a little starch solution. Titrate the excess of the arsenious acid with 0.1 N iodine solution.

Determine the ratio of the arsenite solution to the iodine in the same way as in the above titration. Place 100 ml of arsenite solution in an Erlenmeyer flask, add 10 ml of caustic potash solution, 2 drops of phenolphthalein, hydrochloric acid to decolorization, and then 60 ml of sodium bicarbonate solution. Dilute to the same volume as that of the original experiment and titrate with iodine. If n ml was used in the analysis and n' ml is required in the direct titration of the sodium arsenite solu-

tion then $n' - n$ multiplied by 1.102^1 gives the number of milliliters of chlorine gas at 0°C and 760 mm pressure. In other words,

$$V_0' = (n' - n) \times 1.102$$

However, as the original gas was measured at the temperature t°C and under the pressure B mm, it follows, according to p. 671, that

$$V_0' = \frac{V' \cdot B \cdot 273}{760 \cdot (273 + t)}$$

from which can be computed

$$V' = \frac{V_0' \cdot 760(273 + t)}{B \cdot 273}$$

If V is the original volume of the gas used and R that of the residual gas in the buret, then

$$
\begin{aligned}
Cl_2 + CO_2 + \text{residue} &= V \\
\text{residue} &= R \\
\hline
Cl_2 + CO_2 &= V - R \\
-Cl_2 &= V' \\
\hline
CO_2 &= V - (R + V')
\end{aligned}
$$

and in percentage

$$x = \frac{[V - (R + V')] \cdot 100}{V} = \text{per cent } CO_2$$

Schloetter[2] has described another method for the examination of electrolytic chlorine gas. The chlorine is absorbed by means of hydrazine sulfate, whereby 2 volumes of chlorine set free 1 volume of nitrogen. The carbon dioxide is then absorbed by means of caustic soda solution.

P. Ferchland[3] determines the chlorine by absorption with mercury in the residual gas after the CO_2 has been absorbed with caustic potash. This last method, according to the experiments of Busvold,[4] gives good results; it is to be recommended especially for the analysis of chlorine gas from the Deacon process.

Examination of the Unabsorbed Gas Residue. Usually the residual gas is too small in amount (as in the above case) to examine quantitatively, so that for this part of the analysis a larger sample of the gas

---

[1] This value is derived from the fact that the molar volume of chlorine is 22.04 l. Since Cl_2 corresponds to 2 oxidation equivalents, each milliliter of 0.1 N iodine = 1.102 ml of chlorine gas at 0° and 760 mm.

[2] *Z. angew. Chem*, 1904, 103

[3] *Z. Elektrochem.*, 13, 114.

[4] Inaug. Dissert., Zürich, 1909, also P. Philosophoff, *Chem. Ztg*, 1907, 959.

should be taken. The apparatus shown in Fig. 120 has been used for this purpose with good results. The thick-walled filter bottle A has a capacity of about 1.5 l. It contains about 500 ml of strong caustic

Fig. 120.

potash solution and the absorption tube with stopcock H is fastened air-tight within it.

Manipulation. First fill the absorption tube with the caustic potash solution by suction through H, finally closing H. Then turn the 3-way cock to position II, and, by suction through the left side arm, fill the glass tube with the caustic alkali solution up to the cock. Turn the cock to position I, connect the left side arm, by means of a short piece of rubber tubing and a long piece of glass tubing, with the source of the gas, and aspirate several liters of gas through this tube. As soon as it is safe to assume that all the air has been driven out from the tubing, turn the cock to position II; connect the aspirator at a with flask A, in which a slight vacuum is produced, whereby the gas begins to collect in the absorption tube. Chlorine and carbon dioxide are completely absorbed, while the residual gas collects in the upper part of the absorption tube. Allow the gas to enter the tube until 50–70 ml of the gas residue is obtained; then close cock I, remove the aspirator, drive the gas over into a Hempel gas buret, and analyze according to the methods already described.
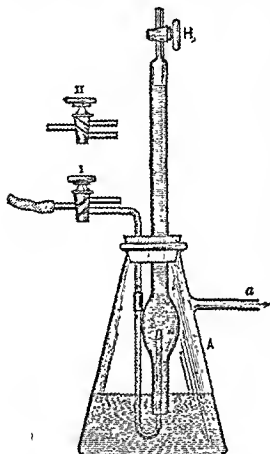
At the carbon electrode (the anode), not only chlorine but also a small amount of oxygen is liberated. The oxygen attacks the carbon of the electrode, forming carbon monoxide, the greater part of which in turn combines with the chlorine, forming phosgene gas, $COCl_2$, but this is decomposed by water with the formation of CO_2 and HCl:

$$COCl_2 + H_2O = CO_2 + 2HCl$$
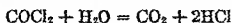
This accounts for the presence of CO_2 and CO in chlorine which has been prepared electrolytically.

2. Hydrochloric Acid, HCl. Mol. Wt. 36.47

Density = 1.2686 (air = 1).[1] Weight of 1 l = 1.6400 g
Molar volume = 22.24 l. Critical temperature = +52°C

Hydrochloric acid is determined in gas mixtures by absorption in standardized alkali hydroxide solution.

3. Sulfur Dioxide. Mol. Wt. 64.06

Density = 2.2639 (air = 1).[2] Weight of 1 l = 2.9267 g
Molar volume = 21.89 l. Critical temperature = +155°C

For the determination of sulfur dioxide from pyrite burners, F. Reich recommends that the gas should be drawn by means of an aspirator through a measured amount of 0.1 N iodine solution, colored blue with starch, until the latter is decolorized. The amount of the gas is equal to the quantity of water which has flowed from the aspirator plus the volume of the absorbed SO_2.

Other examples of gas analyses in which the absorbed constituent is estimated by titration are found in the determination of the hydrogen sulfide in gas mixtures (p. 620) and in the determination of carbonic acid in the atmosphere by the method of Pettenkofer (cf. p. 521).

4. Determination of Ethylene, according to Haber

The principle of this method was discussed on p. 696. The determination can be carried out in the Bunte buret (cf. p. 725, Fig. 118).

First, determine the contents of the lower portion of the buret from the lowest scale division to the cock by weighing the water drawn from between these points, after allowing the buret to drain. Then introduce about 90 ml of the gas to be examined into the buret and take the thermometer and barometer readings. Then, exactly as described on p. 725, draw down the liquid by suction to the stopcock,[3] pour a little bromine water into a small evaporating dish, allow about 10 ml of the liquid to rise into the buret, and, in order to wash the bromine water from the tip into the buret, add 2 or 3 ml of water.

Thoroughly wet the walls of the buret with the bromine water, by suitably turning and inclining the tube; in this way the ethylene is

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[1] Leduc, *Compt. rend.*, **125**, 571 (1897), found the density of hydrogen chloride to be 1.2692, and Busvold, *Inaug. Dissert.*, Zürich, 1910, obtained the value 1.2680. The above figure is the mean of these two determinations.

[2] Leduc, *Compt. rend.*, **117**, 219 (1893).

[3] After about 1 minute liquid will collect above the stopcock, owing to the drainage of the liquid from the sides of the buret; this is removed before adding the bromine.

quickly absorbed. To determine the excess of bromine, allow a strong solution of potassium iodide to rise into the buret and vigorously shake. Run out the liquid into an Erlenmeyer flask, carefully wash the buret with water, and titrate the deposited iodine with 0.1 N sodium thiosulfate solution. Determine the titer of the bromine water by pouring a little into a porcelain dish, pipeting off 10 ml of it, allowing this amount to run into a solution of potassium iodide, and titrating the liberated iodine with 0.1 N sodium thiosulfate solution.

The method of calculating the results will be illustrated best by means of an example.

Example. A gas consisting of 90 volumes of air and 10 volumes of ethylene was used for the analysis. Taken for analysis, 91.2 ml of the mixture. Temperature, 18.3°. Barometer reading, 725 mm. Tension of aqueous vapor at 18.3° = 15.6 mm mercury.

Volume of the ungraduated portion of the buret	6.10 ml
Reading of the bromine water in the graduated part	10.00 ml
Bromine water used	16.10 ml

Ten milliliters of the bromine water corresponds to 12.0 ml 0.1 N sodium thiosulfate solution, so that 16.10 ml of bromine water is equivalent to 19.32 ml of 0.1 N thiosulfate.

We have now:

16.1 ml bromine water	= 19.32 ml 0.1 N solution
16.1 ml bromine water + ethylene	= 12.23 ml 0.1 N solution
The ethylene corresponds to	7.09 ml 0.1 N solution

Since the absorption of the ethylene by the bromine water takes place according to the equation

$$C_2H_4 + Br_2 = C_2H_4Br_2$$
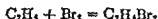
it follows that $2Br = 2I = 20,000$ ml 0.1 N sodium thiosulfate solution $= 22,270[1]$ ml ethylene gas. Since 1 ml 0.1 N sodium thiosulfate corresponds to 1.114 ml C_2H_4, the 7.09 ml of 0.1 N solution used represents $7.09 \times 1.110 = 7.94$ ml C_2H_4 at 0°C and 760 mm pressure, or 9.10 ml C_2H_4 at 18.3°C and 725 mm measured, moist.

$$\left. \begin{array}{l} C_2H_4 = \ 9.1 \\ \text{Air} = 82.1 \\ \hline 91.2 \end{array} \right\} \quad \text{and in per cent} \quad \left\{ \begin{array}{l} C_2H_4 = 10.0 \text{ per cent} \\ \text{Air} = 90.0 \text{ per cent} \\ \hline 100.0 \text{ per cent} \end{array} \right.$$

[1] This method is especially suited for the determination of ethylene present with benzene in illuminating gas. In one sample the sum of the two gases can be determined by absorption with fuming sulfuric acid or bromine water, and in a second sample the ethylene as described above.

[1] Cf. p. 691.

Remark. Instead of using bromine water, which changes its strength so rapidly, it is better to use a tenth-normal solution of potassium bromate; on acidifying, an equivalent quantity of bromine is obtained (cf. p. 629).

The experiment is carried out as follows: Exactly as described above, introduce 90 ml of the gas into the Bunte buret, withdraw the water till the lower cock is reached, place some potassium bromate in a small porcelain dish, draw up about 10 ml of it into the buret, and determine the volume. Then, after wiping off the lower capillary, add an excess of concentrated potassium bromide solution and finally introduce an excess of dilute hydrochloric acid. After shaking 8 minutes, all the ethylene will be brominated. At the end of this time, allow 10 per cent potassium iodide solution to enter the buret, shake and empty into an Erlenmeyer flask. Titrate the iodine thus liberated with 0.1 N sodium thiosulfate solution. The calculation is carried out as before.

5. Determination of Ethylene in the Presence of Acetylene

In one sample determine the sum of the ethylene and acetylene by absorption in fuming sulfuric acid and determine the ethylene by the bromate-bromide absorption method, just described. In the cold, acetylene is not absorbed by dilute bromine water, and this method is suitable for determining ethylene in the presence of small quantities of acetylene. If considerable acetylene is present some acetylene is likely to be absorbed.

The acetylene, however, may be removed by means of a 20 per cent solution of mercuric cyanide in 2 N sodium hydroxide. Use 10 ml of the solution for each 50 ml of the gas mixture. Have the absorbent over the mercury in an absorption pipet. After the removal of the acetylene, ethylene can be removed by the following reagent: Dissolve 20 g $Hg(NO_3)_2$ in 100 ml of 2 N HNO_3 and saturate the solution with $NaNO_3$. Use 5 ml of the absorbent over mercury for the absorption of ethylene. After this benzene can be absorbed in fuming sulfuric acid and then CO, CH_4 and H_2 in the usual way.

GAS-VOLUMETRIC METHODS

If as a result of a chemical reaction a gas is evolved, from the volume of which the weight of the original substance can be computed.

Examples of this sort of an analysis were given under the determination of CO_2 in carbonates (pp. 329, 330, 334, 336), and the NO_3 in nitrates (p. 386).

At this place a few more important determinations of the same nature will be described.

Hydrogen Peroxide Methods

Hydrogen peroxide frequently acts as an *oxidizing* agent; under other conditions it has a marked *reducing* action, and by shaking with inert solids it is decomposed slowly into water and oxygen.

This anomalous behavior can be explained very easily by assuming that one of the oxygen atoms in hydrogen peroxide has one positive and one negative charge as valence bonds.

When hydrogen peroxide decomposes spontaneously on standing, a reaction which is often aided by shaking with an inert substance such as sand, this neutral oxygen atom is lost and oxygen molecules are formed. When hydrogen peroxide acts as an *oxidizing agent*, this neutral oxygen atom is reduced to its normal negative valence of 2. When hydrogen peroxide acts as a *reducing agent*, gaseous oxygen is always one of the products of the reaction. It is usually assumed that half of the evolved oxygen comes from the oxidizing agent and half from the hydrogen peroxide. Thus

$$2MnO_4^- + 5H_2O_2 + 6H^+ = 2Mn^{++} + 8H_2O + 5O_2$$
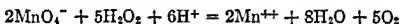
In the two following methods which involve the use of hydrogen peroxide, a large excess of the peroxide should not be used and long-continued shaking should be avoided.

(a) Standardization of Permanganate Solutions

The determination is best made according to Lunge in a gas volumeter (p. 331, Fig. 46). To obtain correct results, however, it is absolutely necessary that no excess of hydrogen peroxide be present. Consequently it is necessary to determine by means of a preliminary experiment the exact value of the permanganate solution in terms of the H_2O_2 solution used (cf. p. 562). Then place a measured amount of the latter in the outside part of the Wagner decomposition bottle (Fig. 46, *a*, p. 331), and add 30 ml of 6 *N* sulfuric acid. After this, introduce the exact amount of hydrogen peroxide required for the decomposition of the permanganate into the inner part of the bottle and connect the bottle with the measuring tube, which is filled with mercury, the cock *b* being removed for the time being, but it is replaced at the end of 2–3 minutes and turned to the position shown in the figure.

Then mix the two liquids, taking care to hold the decomposition flask so that its contents will not be warmed by the heat of the hand, inclining it at an angle of about 90°, and shaking for exactly 1 minute. While the oxygen is being evolved, care must be taken that the gas in the eudiometer is under reduced pressure. After the decomposition

is accomplished, place the gas under atmospheric pressure, close b, and by means of the compensation tube, reduce the volume of the gas to what it would be at 0°C and 760 mm pressure, as described on p. 331.

As the above equation shows, 10 equivalents of $KMnO_4$ furnish 5 moles of oxygen or 5×22.39 l. Hence 1 ml of oxygen gas at 0° and 760 mm corresponds to $1/11.20 = 0.0893$ milliequivalent of $KMnO_4$. If n ml of $KMnO_4$ solution liberates V ml of O_2 the $KMnO_4$ solution is $\frac{V}{n} 0.0893$ normal.

Remark. The volume of permanganate to be taken for the experiment is determined by the size of the measuring tube. If it has a capacity of 150 ml, 15 ml of a 0.2 N solution or 40–50 ml of a 0.1 N solution should be taken.

The hydrogen peroxide used should not be too concentrated; a 2 per cent solution is suitable. The available oxygen present in a sample of pyrolusite[1] can be determined by the same procedure.

(b) Determination of Cerium in Soluble Ceric Salts

If hydrogen peroxide is added to an acid solution of a soluble ceric salt, the salt is reduced with evolution of oxygen:

$$2Ce^{+++} + H_2O_2 = 2Ce^{+++} + 2H^+ + O_2$$
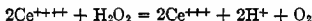
The determination is accomplished in precisely the same way as was described above in the standardization of the permanganate solution. If the volume of liberated oxygen reduced to 0° and 760 mm is multiplied by 0.01537, the product represents the corresponding weight of CeO_2.

Remark. If a large excess of hydrogen peroxide is avoided in the above analysis, satisfactory results will be obtained.

Silicon Fluoride, SiF₄. Mol. Wt. = 104.06

Density = 3.605 (air = 1). Weight of 1 l = 4.660 g
Molar volume = 22.40 l

Determination of Fluorine as Silicon Fluoride (Hempel and Oettel)[2]

Principle. If a mixture of calcium fluoride and powdered quartz is treated with concentrated sulfuric acid in a glass vessel, all the fluorine will be expelled as silicon fluoride:

$$2CaF_2 + SiO_2 + 2H_2SO_4 = 2CaSO_4 + 2H_2O + SiF_4$$
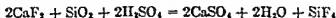
and this gas can be collected and measured.

One milliliter SiF₄ at 0° and 760 mm pressure corresponds to 0.006971 g CaF_2, or 0.003393 g F_2.

[1] Lunge's *Alkali Makers' Handbook*.
[2] *Gasanalytische Methoden*.

Procedure. Mix a weighed amount of the very finely powdered substance, which must not contain any other acid that can be expelled by treatment with concentrated sulfuric acid,[1] with 3 g of finely powdered ignited quartz, and introduce into the dry decomposition flask K (Fig. 121). Evacuate the flask somewhat by twice lowering the leveling tube N with the stopcock H open, closing the cock and expelling the air. At the beginning of the experiment, the buret H should not be connected with the Orsat tube O. By raising the ground-

Fig. 121.

glass tube R, cause about 30 ml of concentrated sulfuric acid to flow into the flask. This acid must have been previously heated in a porcelain crucible for some time at a temperature near the boiling point, to destroy every trace of organic matter, and allowed to cool in a desiccator over phosphorus pentoxide. Heat the acid in K to boiling with the stopcock H open, and frequently shake. During the entire experiment, keep the mercury level in the tube N a little lower than that of the mercury in the measuring tube M.[2]

At first the sulfuric acid foams considerably, but soon ceases, which is a sure sign that the decomposition is complete. Then remove the flame, allow the sulfuric acid to cool, and expel all the gas in K by introducing through V sulfuric acid, which has been previously heated and cooled as described above. As soon as the sulfuric acid reaches the stopcock H, close it. After waiting 10 minutes more, place the gas under atmospheric pressure, by suitably raising N, and note the volume and temperature.

Now drive the gas over into the Orsat tube O, containing caustic potash solution (1:2). The silicon tetrafluoride is immediately absorbed. Return the residual gas to the tube M, and after waiting 15 minutes read the volume. The difference between the two readings gives the volume of silicon tetrafluoride.

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[1] Cf. pp. 404, 405.

[2] To keep the inside of N perfectly dry, place 2-3 ml of concentrated sulfuric acid on top of the mercury.
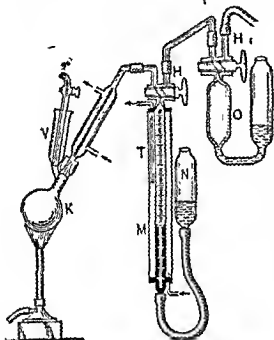
Remarks. A. Koeb tested this method in the Zürich laboratory and obtained results varying from 98.97 to 102 63 per cent with pure calcium fluoride. To obtain this accuracy, however, it is necessary to carry out the decomposition under approximately atmospheric pressure. When working under a vacuum the results were always too low. Thus in one experiment only 85.70 per cent of the theoretical value was obtained.

During these experiments with reduced pressure, a white sublimate formed at the lower part of the condenser, which, on coming in contact with the sulfuric acid that is introduced at the last, caused a strong effervescence. Since all the gas in the buret was replaced, however, we believed that the low results could be traced to the absorption of silicon fluoride by the sulfuric acid This idea proved to be false, for a measured volume of silicon fluoride does not change when allowed to stand for 24 hours over concentrated sulfuric acid. The error, therefore, must be caused by the deposit that has condensed in the lower part of the condenser. If the work is carried out under atmospheric pressure as described above, the white deposit is never obtained.

The method can be used for the estimation of fluorine in the presence of carbonates. In this case the silicon fluoride is absorbed by means of a little water and the carbon dioxide by means of caustic potash. However, as a little of the carbon dioxide is dissolved by the water, the gas residue which has been freed from carbon dioxide is shaken with this water again, whereby this dissolved carbon dioxide is removed and can be absorbed by a further treatment with caustic potash solution. For further details, consult the original paper by Hempel and Scheffler.[1]

Determination of Water Vapor in Gas Mixtures

In gas analysis it is a common practice to express the results in percentages by volume. Thus if a mixture of oxygen and carbon dioxide measures V_1 ml under atmospheric pressure and after the carbon dioxide has been absorbed the residual gas measures V_2 ml under the same pressure, it is customary to assume that the original gas contained $V_1 - V_2$ ml of CO_2 and V_2 ml of oxygen. A little consideration will show that this is really an inexact assumption although it is true that the original mixture could be obtained by mixing the indicated volumes of carbon dioxide and oxygen.

When two or more gases are mixed, each occupies the total volume of the mixture. This is an apparent contradiction because two bodies cannot occupy the same space. With a gas, however, the actual volume taken up by the molecules is very small compared to the total volume occupied by the gas, and it is customary to neglect it in gas analysis. Thus at 0° and 1 mm pressure, 1 l of hydrogen gas contains only 0.16 ml of space actually occupied by hydrogen molecules. Under higher pressures, the actual volume occupied by the molecules becomes less.

In V ml of carbon dioxide and oxygen under atmospheric pressure, therefore, there are present V ml of carbon dioxide and V ml of oxygen,

[1] *Z. anorg. Chem.*, **20**, 1 (1897).

and the pressure of the mixture is the combined pressures of the two gases. In any gas mixture, *the total pressure is the sum of the partial pressures.*

In a mixture of two gases, the percentage composition can be easily computed if the volume of the gas mixture is known under a definite pressure and temperature, and, at the same time, the partial pressure of one of the gases is known. Moreover, the ratio of the partial pressures of the gases shows the relative volumes provided that the gases were measured singly under the same pressure and at the same temperature.

Applications. 1. *Reduction of Volumes of Moist Gases to a Dry Condition at 0° and 760 mm.* If a gas is saturated with water vapor at any temperature, the partial pressure exerted by the water is known. Water evaporates until the vapor pressure of the liquid water is exactly balanced by the gas pressure exerted by the evaporated water and this is independent of whether other gases are present or not. The table on pp. 751–753 gives the vapor pressures of water at various temperatures. If a gas saturated with water vapor occupies a volume V_t at $t°$ and P mm pressure (of liquid mercury) and w is the tension of aqueous vapor at this temperature, then the volume occupied by the dry gas at 0° and 760 mm pressure would be $V_0 = V_t \dfrac{(P - w)273}{760(273 + t)}$.

2. *Calculation of the Moisture in the Air at Normal Pressure (760 mm) and Temperature $t°$.*

What is the percentage of moisture (by volume) of air saturated with moisture at 0°, 25°, and 35°? According to the table: $w_0 = 4.6$ mm; $w_{25} = 23.5$ mm; and $w_{35} = 41.8$ mm. By dividing each of these values by 760 and multiplying by 100, we find the percentage of moisture to be 0.61 per cent at 0°, 3.09 per cent at 25°, and 5.50 per cent at 35°.

If the gas is not saturated with moisture, the relation of the dry gas to the moist one can be computed if the degree of saturation, or *humidity*, is known. The humidity of the gas expresses the amount of moisture as a percentage of the amount that the gas contains when saturated with moisture. Thus, if the humidity is 50 per cent, the gas could take up just as much more water at the prevailing temperature. If the humidity is r, then, if the given gas were measured dry at 760 mm and at the same temperature, its volume would be $\dfrac{V(P - r \cdot w)}{760}$; and if the water exists as gas at 760 mm pressure and the same temperature, its volume is $\dfrac{V \cdot r \cdot w}{760}$.

3. *Calculation of the Weight of Water Vapor in a Given Volume of Air, at $t°$ and P mm pressure, which is saturated with moisture.*

If 1 ml of water exists as a gas at $0°$ and 760 mm pressure, it ought to weigh 0.000801 g as an ideal gas. At $t°$ and P mm pressure, it should weigh

$$\frac{0.000801 \times P \times 273}{760 \times (273 + t)} \text{ g}$$

If the gas is not saturated with water vapor, but the degree of saturation (the humidity) is known, then the following formula gives the weight of water vapor present in the volume v_t of the gas:

$$\frac{0.00801 \cdot r \cdot w \cdot v_t \cdot 273}{760(273 + t)} \text{ g}$$

Or, if the weight of vapor present in a given gas volume is known, then from the last equation the humidity, r, of gas may be computed:

$$r = \frac{g \cdot 760(273 + t)}{0.000801 \cdot w \cdot v_t \cdot 273}$$

Density Tables

One of the easiest methods for determining the percentage composition of a solution containing only one dissolved substance is to determine the density of the solution. This, however, is not a reliable method of analysis because the density of a solution is never strictly proportional to the quantity of dissolved substance, and if a density curve is plotted for all possible concentrations, it will sometimes be found that there are, at certain parts of the curve, two different concentrations that have the same density.

Instead of determining the *density* of a solution, or weight of the unit volume in a vacuum, it is often customary to determine the weight of the solution as compared to the weight of the same volume of another liquid. Water is commonly taken as the basis of comparison, and since 1 ml of water at $4°$ weighs 1 g, the specific gravity when referred to water at this temperature is the same as the density, when this is defined as the weight in grams of 1 ml of water.

Unfortunately, however, usage has not been uniform in the choice of temperature at which the specific gravities have been taken, and the comparison is often made with water at the same temperature.

The extensive application of hydrometers as measuring instruments in the collection of revenues in commerce and for buying and selling certain liquids has led the National Bureau of Standards to define the

various scales in terms of fundamental units. Some of the tables in this book are taken from this source. Some years ago the Manufacturing Chemists' Association of the United States published tables, which have been copied in quite a number of textbooks, in which the specific gravities were taken at 60°F and referred to water at the same temperature.

Whenever a specific gravity value is given, the *modulus* should also be stated. Thus a specific gravity at $\frac{60°}{60°}$ F means that the comparison was made at 60°F with water at the same temperature, and $\frac{15°}{4°}$ C means that the comparison was made at 15°C with water at 4°C.

The confusion, however, does not end here. Just as certain civilized countries, particularly England and the United States, have been slow to adopt the metric system, so the people of most countries have held tenaciously to other scales for determining relative masses of equal volumes of liquids. Thus the English Twaddell scale and the various French Baumé scales are still in constant use. Throughout the text of this book, the metric system has been used for the sake of simplicity, and, as far as the analytical chemist is concerned, density tables are, on the whole, more satisfactory than specific-gravity tables. Data will be given, however, showing how these tables can be translated into other units.

PART IV. TABLES

DENSITY OF STRONG ACIDS AT 15° IN VACUO

(According to LUNGE, ISLER, NAEF, and MARCHLEWSKY)*

In determining the weight in the air of a given volume of acid or base in this and the following tables, it must be remembered that the values here are made with allowance for the buoyancy of air (cf pp. 13–15, 435–437).

Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight			Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight	
	HCl	HNO₃	H₂SO₄		HNO₃	H₂SO₄
1.000	0.16	0.10	0 09	1.235	37.51	31.70
1.005	1.15	1.00	0.95	1.240	38.27	32.23
1.010	2.14	1.90	1 57	1.245	39.03	32.86
1.015	3.12	2.80	2 30	1.250	39.80	33.43
1.020	4 13	3.70	3 03	1.255	40.56	34.00
1.025	5.15	4 60	3 76	1.260	41.32	34.57
1.030	6 15	5 50	4.49	1.265	42 08	35.14
1.035	7.15	6 38	5.23	1 270	42.85	35.71
1.040	8.16	7.26	5.96	1.275	43 62	36.29
1.045	9.16	8 13	6.67	1.280	44.39	36.87
1.050	10.17	8 99	7.37	1.285	45.16	37.45
1.055	11.18	9.84	8.07	1.290	45.93	38.03
1.060	12.19	10 67	8.77	1.295	46.70	38.61
1 065	13.19	11.50	9.47	1.300	47.47	39.19
1.070	14.17	12 32	10.10	1.305	48.24	39.77
1 075	15.16	13.14	10 90	1.310	49 05	40 35
1.080	16.15	13 94	11 60	1.315	49 88	40 93
1 085	17.13	14.73	12 30	1.320	50.69	41.50
1.090	18.11	15 52	12 99	1 325	51.51	42 08
1.095	19 06	16 31	13 67	1 330	52.34	42.66
1.100	20 01	17.10	14 35	1.335	53.17	43.20
1.105	20 97	17.88	15.03	1.340	54.04	43.74
1.110	21 92	18 66	15.71	1.345	54.90	44.28
1.115	22 86	19.44	16 36	1.350	55.76	44.82
1.120	23 82	20 22	17.01	1.355	56 63	45.35
1.125	24.78	20.99	17.66	1.360	57 54	45.88
1.130	25 73	21.76	18 31	1.365	58.45	46.41
1.135	26 70	22 53	18.96	1.370	59.36	46.94
1.140	27 66	23 30	19 61	1.375	60.27	47.47
1.145	28.61	24 07	20 26	1.380	61 24	48.00
1.150	29 57	24 83	20 91	1.385	62.21	48.53
1.155	30.55	25 59	21.55	1.390	63.20	49.06
1.160	31.52	26.35	22.19	1.395	64.22	49.59
1.165	32.49	27.11	22.83	1.400	65.27	50.11
1.170	33 46	27 87	23 47	1.405	66.37	50.63
1.175	34.42	28.62	24.12	1 410	67.47	51.15
1.180	35 39	29 37	24 76	1.415	68.60	51.66
1.185	36.31	30.12	25.40	1.420	69 77	52.15
1.190	37.23	30.87	26 04	1.425	70.95	52.63
1.195	38.16	31.62	26 68	1 430	72.14	53.11
1.200	39.11	32.34	27.32	1 435	73 35	53.59
1.205		33 07	27 05	1.440	74.64	54.07
1.210		33 80	28 58	1.445	75.94	54.55
1.215		34.53	29 21	1 450	77.24	55 03
1.220		35 26	29 84	1.455	78.56	55.50
1.225		36 01	30.48	1.460	79.91	55.97
1.230		36.76	31.11	1.465	81.38	56.43

* Lunge-Berl. *Chem. tecle. Untersuchungsmethoden.*

DENSITY OF STRONG ACIDS AT 15° IN VACUO — Continued

Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight	
	HNO₃	H₂SO₄
1.470	82.86	
1.475	84.41	56.90
1.480	85.01	57.37
1.485	87.66	57.83
1.490	89.86	58.28
1.495	91.56	58.74
1.500	94.94	59.22
1.505	95.34	59.70
1.510	98.05	60.18
1.515	99.02	60.65
1.520	99.62	61.12
1.525		61.59
1.530		62.06
1.535		62.53
1.540		63.00
1.545		63.43
1.550		63.85
1.555		64.26
1.560		64.67
1.565		65.20
1.570		65.65
1.575		66.09
1.580		66.53
1.585		66.95
1.590		67.40
1.595		67.83
1.600		68.26
1.605		68.70
		69.13

Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight
	H₂SO₄
1.510	69.56
1.615	70.00
1.620	70.42
1.625	70.85
1.630	71.27
1.635	71.70
1.640	72.12
1.645	72.55
1.650	72.96
1.655	73.40
1.660	73.81
1.665	74.24
1.670	74.66
1.675	75.08
1.680	75.50
1.685	75.94
1.690	76.38
1.695	76.76
1.700	77.17
1.705	77.60
1.710	78.04
1.715	78.48
1.720	78.92
1.725	79.36
1.730	79.80
1.735	80.24
1.740	80.68
1.745	81.12

Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight
	H₂SO₄
1.750	81.56
1.755	82.00
1.760	82.44
1.765	83.01
1.770	83.51
1.775	84.02
1.780	84.50
1.785	85.10
1.790	85.70
1.795	86.30
1.800	86.92
1.805	87.60
1.810	88.30
1.815	89.16
1.820	90.05
1.825	91.00
1.830	92.10
1.835	93.56
1.840	95.60
1.8405	95.95
1.8410	96.38
1.8415	97.35
1.8410	98.20
1.8405	98.52
1.8400	98.72
1.8395	98.77
1.8390	99.12
1.8385	99.31

DENSITY OF POTASSIUM AND SODIUM HYDROXIDE
SOLUTIONS AT 15° C

Specific Gravity	Per Cent KOH	Per Cent NaOH	Specific Gravity	Per Cent KOH	Per Cent NaOH
1.007	0.9	0.59	1.252	27.0	22.50
1.014	1.7	1.20	1.263	28.2	23.50
1.022	2.6	1.65	1.274	28.9	24.48
1.029	3.5	2 50	1.285	29.8	25.50
1.037	4.5	3.22	1.297	30.7	26.58
1.045	5.6	3.79	1.308	31.8	27.65
1.052	6.4	4.50	1.320	32.7	28.83
1.060	7.4	5 20	1.332	33.7	30.00
1.067	8.2	5.86	1 345	34.9	31 20
1.075	9.2	6 53	1 357	35.9	32.50
1.083	10.1	7.30	1.370	36.9	33.73
1.091	10.9	8.07	1 383	37.8	35.00
1.100	12.0	8.78	1.397	38.9	36.36
1.108	12.9	9 50	1.410	39.9	37.65
1.116	13.8	10.30	1.424	40.9	39.06
1.125	14.8	11 06	1.438	42.1	40.47
1.134	15.7	11.90	1.453	43.4	42.02
1.142	16.5	12.69	1.468	44.6	43.58
1.152	17.6	13 50	1.483	45.8	45.16
1.162	18.6	14 35	1.498	47.1	47.73
1.171	19.5	15.15	1.514	48.3	48.41
1.180	20.5	16 00	1.530	49.4	50.10
1.190	21.4	16.91	1.546	50.6	.....
1.200	22.4	17.81	1.563	51.9	.....
1.210	23.3	18.71	1.580	53.2	.....
1.220	24.2	19.65	1.597	54.5	.....
1.231	25.1	20.99	1.615	55.9	.....
1.241	26.1	21.55	1.634	57.5	.....

DENSITY TABLES

DENSITY OF AMMONIA SOLUTIONS AT 15° C
(According to LUNGE and WIERNIK)*

Specific Gravity	Per Cent NH₄	Specific Gravity	Per Cent NH₃
1.000	0.00	0.940	15.63
0.998	0.45	0.938	16.22
0.996	0.91	0.936	16.82
0.994	1.37	0.934	17.42
0.992	1.84	0.932	18.03
0.990	2.31	0.930	18.64
0.988	2.80	0.928	19.25
0.986	3.30	0.926	19.87
0.984	3.80	0.924	20.49
0.982	4.30	0.922	21.12
0.980	4.80	0.920	21.75
0.978	5.30	0.918	22.39
0.976	5.80	0.916	23.03
0.974	6.30	0.914	23.68
0.972	6.80	0.012	24.33
0.970	7.31	0.910	24.99
0.968	7.82	0.908	25.65
0.965	8.33	0.906	26.31
0.964	8.84	0.904	26.98
0.962	9.35	0.902	27.65
0.960	9.91	0.900	28.33
0.958	10.47	0.898	29.01
0.956	11.03	0.896	29.69
0.954	11.60	0.894	30.37
0.952	12.17	0.892	31.05
0.950	12.74	0.890	31.75
0.948	13.31	0.888	32.60
0.946	13.88	0.886	33.25
0.944	14.46	0.884	34.10
0.942	15.04	0.852	34.95

* Lunge-Berl. *Chem. techn. Untersuchungsmethoden.*

TENSION OF WATER VAPOR ACCORDING TO REGNAULT

Degrees, C	Tension in Millimeters	Degrees, C	Tension in Millimeters	Degrees, C	Tension in Millimeters
−2.0	3.955	+2.0	5.302	+6.0	6.998
1.9	3.985	2.1	5.340	6.1	7.047
1.8	4.016	2.2	5.378	6.2	7.095
1.7	4.047	2.3	5.416	6.3	7.144
1.6	4.078	2.4	5.454	6.4	7.193
1.5	4.109	2.5	5.491	6.5	7.242
1.4	4.149	2.6	5.530	6.6	7.292
1.3	4.171	2.7	5.569	6.7	7.342
1.2	4.203	2.8	5.608	6.8	7.392
1.1	4.235	2.9	5.647	6.9	7.442
1.0	4.267	3.0	5.687	7 0	7.492
0.9	4.299	3.1	5.727	7.1	7.544
0 8	4.331	3.2	5.767	7.2	7.595
0.7	4.364	3.3	6 807	7.3	7.647
0.6	4.397	3.4	5.848	7.4	7.699
0.6	4 430	3.5	5.889	7.6	7.751 ·
0.4	4.463	3.6	5.930	7.6	7.804
0.3	4.497	3.7	5 972	7.7	7.857
0.2	4.531	3.8	6.014	7.8	7.910
0.1	4.565	3.9	6.055	7.9	7.964
0.0	4.600	4 0	6.097	8.0	8.017
+0.1	4.633	4.1	6.140	8.1	8.072
0.2	4.667	4.2	6 183	8.2	8.126
0.3	4.700	4.3	6.226	8.3	8.181
0.4	4.733	4.4	6.270	8.4	8.236
0.6	4.767	4 5	6.313	8.5	8.291
0.6	4.801	4.6	6.357	8 6	8.347
0.7	4.836	4.7	6.401	8.7	8.401
0.8	4 871	4.8	6.445	8.8	8.461
0.9	4.905	4.9	6.490	8.9	8.517
1.0	4.940	5 0	6.534	9 0	8.574
1.1	4.975	5.1	6.580	9.1	8.632
1.2	5.011	5.2	6 625	9.2	8.690
1.3	5.047	5 3	6.671	9.3	8.748
1.4	6.082	5.4	6.717	9.4	8.807
1.5	5.118	5 5	6.763	9.5	8.865
1.6	5 155	5.6	6.810	9.6	8.925
1.7	5.191	5 7	6 857	9.7	8.985
1.8	5.228	5.8	6.904	9.8	9.045
1.9	5.265	5.9	6.951	9.9	9.105

TENSION OF WATER VAPOR ACCORDING TO REGNAULT — *Continued*

Degrees, C	Tension in Millimeters	Degrees, C	Tension in Millimeters	Degrees, C	Tension in Millimeters
+10.0		+14.0		+18.0	
10.1	9.165	14.1	11.908	18.1	15.357
10.2	9.227	14.2	11.989	18.2	15.454
10.3	9.288	14.3	12.064	18.3	15.552
10.4	9.350	14.4	12.142	18.4	15.650
	9.412		12.220		15.747
10.5		14.5		18.5	
10.6	9.474	14.6	12.298	18.6	15.845
10.7	9.537	14.7	12.378	18.7	15.945
10.8	9.601	14.8	12.458	18.8	16.045
10.9	9.665	14.9	12.538	18.9	16 145
	9.728		12.619		16.246
11.0		15.0		19.0	
11.1	9.792	15.1	12.699	19.1	16.346
11.2	9.857	15.2	12.781	19.2	16.449
11.3	9.923	15.3	12.864	19.3	16.552
11.4	9.989	15.4	12.947	10.4	16.655
	10.054		13.029		16.758
11.5		15.5		19.5	
11.0	10.120	15.6	13.112	19.6	16 861
11.7	10.187	15.7	13.107	19.7	16.967
11.8	10.255	15.8	13.281	19.8	17.073
11.9	10.322	15.9	13.366	19.0	17.179
	10.389		13.451		17.235
12.0		16.0		20.0	
12.1	10.457	16.1	13.536	20.1	17.391
12.2	10.526	16.2	13.623	20.2	17.500
12.3	10.596	16.3	13.710	20.3	17.603
12.4	10.665	16.4	13.797	20.4	17.717
	10.734		13.885		17.826
12.5		16.5		20.5	
12.6	10.801	16.6	13.972	20.6	17.935
12.7	10.875	16.7	14.062	20.7	18.047
12.8	10.947	16.8	14.151	20.8	18.159
12.9	11.019	16.9	14 241	20.9	18.271
	11.090		14.331		18.383
13.0		17.0		21.0	
13.1	11.162	17.1	14.421	21.1	18.495
13.2	11.235	17.2	14.513	21.2	18.610
13.3	11.309	17.3	14.605	21.3	18.724
13.4	11.383	17.4	14.697	21.4	18.839
	11.456		14 790		18.954
13.5		17.5		21.5	
13.6	11.530	17.6	14.882	21.6	19.069
13.7	11.605	17.7	14.977	21.7	19.187
13.8	11.681	17.8	15.072	21.8	19.305
13.9	11.757	17.9	15.167	21 9	19.423
	11.832		15.262		19.541

TENSION OF WATER VAPOR ACCORDING TO REGNAULT—*Concluded*

Degrees, C	Tension in Millimeters	Degrees, C	Tension in Millimeters	Degrees, C	Tension in Millimeters
+22 0	19.659	+26.5	25 738	+31.0	33.405
22 1	19.780	26 6	25.891	31.1	33 596
22.2	19.901	26 7	26 045	31.2	33.787
22 3	20.022	26 8	26.198	31.3	33.980
22.4	20.143	26.9	26.351	31.4	34 174
22 5	20 265	27.0	26 505	31.5	34.368
22 6	20.389	27 1	26.663	31.6	34 564
22 7	20 514	27 2	26.820	31.7	34 761
22 8	20 639	27 3	26.978	31.8	34 959
22 9	20.763	27.4	27 136	31.9	35.159
23 0	20 888	27 5	27.294	32.0	35.359
23 1	21 016	27 6	27 455	32.1	35.559
23.2	21 144	27 7	27.617	32.2	35 760
23.3	21 272	27 8	27.778	32.3	35.962
23 4	21.400	27.9	27.939	32.4	36.165
23.5	21.528	28.0	28 101	32.5	36.370
23 6	21 659	28 1	28 267	32.6	36.576
23.7	21 790	28 2	28 433	32.7	36.783
23.8	21 921	28 3	28 599	32.8	36.991
23.9	22 053	28.4	28.765	32.9	37.200
24 0	22 184	28 5	28 931	33 0	37.410
24 1	22 319	28 6	29 101	33.1	37 621
24 2	22 453	28 7	29 271	33.2	37.832
24.3	22 588	28 8	29 441	33 3	38 045
24.4	22 723	28.9	29 612	33.4	38.258
24 5	22 858	29 0	29.782	33.5	38 473
24.6	22 996	29 1	29 956	33 6	38.689
24.7	23 135	29 2	30 131	33 7	38.906
24 8	23 273	29 3	30 305	33 8	39.124
24.9	23 411	29 4	30 479	33 9	39.344
25.0	23 550	29 5	30 654	34.0	39.565
25 1	23 692	29 6	30 833	34 1	39 786
25.2	23 834	29.7	31 011	34 2	40.007
25 3	23 976	29 8	31 190	34 3	40.230
25.4	24.119	29 9	31.369	34 4	40.455
25.5	24 261	30 0	31.548	34.5	40 680
25.6	24 406	30 1	31.729	34 6	40.907
25.7	24 552	30 2	31.911	34 7	41.135
25.8	24 697	30 3	32.091	34.8	41.364
25.9	24.842	30 4	32.278	34.0	41.595
26.0	24.988	30 5	32.463	35.0	41.827
26.1	25 138	30.6	32.650		
26 2	25.288	30 7	32 837		
26 3	25 438	30 8	33 026		
26.4	25.588	30.9	33 215		

HEATS OF COMBUSTION OF 1 L OF GAS MEASURED AT 0° AND 760 MM BAROMETRIC PRESSURE

Gas	Weight of 1 L in Grams	Referred to	
		Gaseous Water Calories	Liquid Water Calories
Carbon monoxide.............	1.25016	2,560	3,034
Hydrogen.....................	0.09004	2,595	3,077
Methane......................	0.71483	8,505	9,469
Ethylene......................	1.25399	14,018	14,989
Propylene.....................	1.93660	21,226	22,720
Benzene gas...................	3 48428	(?)33,750	(?)35,198
Acetylene.....................	1.18080	13,682	14,073
Generator gas.................	....	about 900	about 1,000
Water gas.....................	....	" 3,386	" 3,700
Dowson gas...................	....	" 1,400	....
Illuminating gas..............	....	" 5,000	" 5,500

The values in the above table are based upon Thomsen's measurements and only in the case of benzene is the theoretical density used.*

STANDARD TEMPERATURES

At the seventh General Conference on Weights and Measures the following standard temperatures were adopted for preparing an international temperature scale.

Boiling point of oxygen...................... ....—182.97° C
Melting point of ice. 0.00
Boiling point of water....... .... 100.00
Boiling point of sulfur 444.60
Melting point of silver..... .... 960.5
Melting point of gold............... 1063

* Julius Thomsen, *Thermochem. Untersuchungen* (1882), Vol. II, pp. 56, 85, 107, and Vol. IV, p. 254.

$$CO + O = CO_2 + 67{,}960 \text{ cals.}$$
$$H_2 + O = H_2O + 68{,}357 \text{ cals}$$
$$CH_4 + 4O = 2H_2O + CO_2 + 211{,}930 \text{ cals.}$$
$$C_2H_4 + 6O = 2H_2O + 2CO_2 + 333{,}350 \text{ cals.}$$
$$C_3H_6 + 9O = 3H_2O + 3CO_2 + 492{,}740 \text{ cals.}$$
$$C_6H_6 + 15O = 3H_2O + 6CO_2 + 787{,}950 \text{ cals.}$$
$$C_2H_2 + 5O = H_2O + 2CO_2 + 310{,}450 \text{ cals.}$$
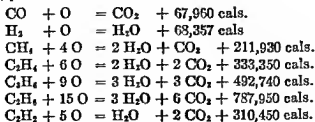
MELTING POINTS OF THE CHEMICAL ELEMENTS*

Element	C	F	Element	C	F
Helium	<−271	<−456	Neodymium	840?	1544
Hydrogen	−259	−434	Arsenic	850?	1562
Neon	−253?	−423	Barium	850	1562
Fluorine	−223	−369	Praseodymium	940?	1724
Oxygen	−218	−360	Germanium	958	1756
Nitrogen	−210	−346	Silver	960.5	1761
Argon	−188	−306	Gold	1063.0	1945.5
Krypton	−169	−272	Copper	1083.0	1981.5
Xenon	−140	−220	Manganese	1260	2300
Chlorine	−101.5	−150.7	Samarium	1300−1400	2370−2550
Mercury	−38.9	−38.0	Beryllium (glucinum)	1350?	2462
Bromine	−7.3	+18.9	Scandium	?	
Cesium	+26	79	Silicon	1420	2588
Gallium	30	86	Nickel	1452	2646
Rubidium	38	100	Cobalt	1480	2696
Phosphorus	44	111.2	Yttrium	1490	2714
Potassium	62.3	144	Chromium	1520	2768
Sodium	97.5	207.5	Iron	1530	2786
Iodine	113.5	236.3	Palladium	1549	2820
Sulfur (S$_I$)	112.8	235.0	Zirconium	1700?	3090
(S$_{II}$)	119.2	246.6	(Niobium)	1700?	3090
(S$_{III}$)	106.8	224.2	Thorium	{ > 1700 < Pt	{ > 3090 < Pt
Indium	155	311	Vanadium	1720	3128
Lithium	186	367	Platinum	1755	3191
Selenium	217−220	422−428	Ytterbium	?	
Tin	231.9	449.4	Titanium	1800	3272
Bismuth	271	520	Uranium	<1850	<3362
Thallium	302	576	Rhodium	1950	3542
Cadmium	320.9	609.6	Boron	2200−2500?	4000−4500
Lead	327.4	621.3	Iridium	2350?	4262
Zinc	419.4	786.9	Ruthenium	2450?	4442
Tellurium	452	846	Molybdenum	2500?	4500
Antimony	630.0	1166	Osmium	2700?	4900
Cerium	640	1184	Tantalum	2850	5160
Magnesium	651	1204	Tungsten	3000	5430
Aluminum	658.7	1217.7	Carbon	{ >3600 for p=1at.	{ >6500 for p=1at.
Radium	700	1292			
Calcium	810	1490			
Lanthanum	810?	1490			
Strontium	>Ca<Ba?				

* Reproduced from Circular 35 (2nd edition) of National Bureau of Standards.

APPROXIMATE TEMPERATURES BY COLORS

	Cent.	Fahr.
First visible red	525	977
Dull red	700	1292
Cherry red	900	1652
Dull orange	1100	2012
White	1300	2372
Dazzling white	1500	2732

DENSITY OF PHOSPHORIC ACID AT 17.5°

Specific Gravity	Per Cent P₂O₅	Per Cent H₃PO₄	Specific Gravity	Per Cent P₂O₅	Per Cent H₃PO₄	Specific Gravity	Per Cent P₂O₅	Per Cent H₃PO₄
1.809	68.0	93.57	1.462	46.0	63.37	1.208	24.0	33.06
1.800	67.5	92.99	1.455	45.5	62.68	1.203	23.5	32.37
1.792	67.0	92.30	1.448	45.0	61.99	1.198	23.0	31.68
1.783	66.5	91.61	1.441	44.5	61.30	1.193	22.5	30.99
1.775	66.0	90.92	1.435	44.0	60.61	1.188	22.0	30.31
1.766	65.5	90.23	1.428	43.5	59.92	1.183	21.5	29.62
1.758	65.0	89.54	1.422	43.0	59.23	1.178	21.0	28.93
1.750	64.5	88.85	1.415	42.5	58.55	1.174	20.5	28.24
1.741	64.0	88.16	1.409	42.0	57.86	1.169	20.0	27.55
1.733	63.5	87.43	1.402	41.5	57.17	1.164	19.5	26.86
1.725	63.0	86.79	1.396	41.0	56.48	1.159	19.0	26.17
1.717	62.5	86.10	1.389	40.5	55.79	1.155	18.5	25.48
1.709	62.0	85.41	1.383	40.0	55.10	1.150	18.0	24.80
1.701	61.5	84.72	1.377	39.5	54.41	1.145	17.5	24.11
1.693	61.0	84.03	1.371	39.0	53.72	1.140	17.0	23.42
1.685	60.5	83.34	1.365	38.5	53.04	1.135	16.5	22.73
1.677	60.0	82.65	1.359	38.0	52.35	1.130	16.0	22.04
1.669	59.5	81.97	1.354	37.5	51.66	1.126	15.5	21.35
1.661	59.0	81.28	1.348	37.0	50.97	1.122	15.0	20.66
1.653	58.5	80.59	1.342	36.5	50.28	1.118	14.5	19.97
1.645	58.0	79.90	1.336	36.0	49.59	1.113	14.0	19.28
1.637	57.5	79.21	1.330	35.5	48.90	1.109	13.5	18.60
1.629	57.0	78.52	1.325	35.0	48.21	1.104	13.0	17.91
1.621	56.5	77.83	1.319	34.5	47.52	1.100	12.5	17.22
1.613	56.0	77.14	1.314	34.0	46.84	1.096	12.0	16.53
1.605	55.5	76.45	1.308	33.5	46.15	1.091	11.5	15.84
1.597	55.0	75.77	1.303	33.0	45.46	1.087	11.0	15.15
1.589	54.5	75.08	1.298	32.5	44.77	1.083	10.5	14.46
1.581	54.0	74.39	1.292	32.0	44.08	1.079	10.0	13.77
1.574	53.5	73.70	1.287	31.5	43.39	1.074	9.5	13.09
1.566	53.0	73.01	1.281	31.0	42.70	1.070	9.0	12.40
1.559	52.5	72.32	1.276	30.5	42.01	1.066	8.5	11.71
1.551	52.0	71.63	1.271	30.0	41.33	1.062	8.0	11.02
1.543	51.5	70.94	1.265	29.5	40.64	1.058	7.5	10.33
1.536	51.0	70.26	1.260	29.0	39.95	1.053	7.0	9.64
1.528	50.5	69.57	1.255	28.5	39.26	1.049	6.5	8.95
1.521	50.0	68.88	1.249	28.0	38.57	1.045	6.0	8.26
1.513	49.5	68.19	1.244	27.5	37.88	1.041	5.5	7.57
1.505	49.0	67.50	1.239	27.0	37.19	1.037	5.0	6.89
1.498	48.5	66.81	1.233	26.5	36.50	1.033	4.5	6.20
1.491	48.0	66.12	1.228	26.0	35.82	1.029	4.0	5.51
1.484	47.5	65.43	1.223	25.5	35.13	1.025	3.5	4.82
1.476	47.0	64.75	1.218	25.0	34.44	1.021	3.0	4.13
1.469	46.5	64.06	1.213	24.5	33.75	1.017	2.5	3.44

DENSITY OF ACETIC ACID AT 15°

Specific Gravity	Per Cent H C₂H₃O₂	Specific Gravity	Per Cent H C₂H₄O₄	Speac Gravity	Per Cent H.C₂H₃O₂	Specific Gravity	Per Cent H.C₂H₄O
0.9992	0	1 0363	26	1.0623	51	1 0747	76
1.0007	1	1.0375	27	1.0631	52	1 0748	77
1.0022	2	1.0388	28	1.0638	53	1.0748	78
1.0037	3	1.0400	29	1.0646	54	1.0748	79
1.0052	4	1 0412	30	1 0653	55	1.0748	80
1 0067	5	1.0424	31	1 0660	56	1.0747	81
1 0083	6	1.0436	32	1.0666	57	1 0746	82
1.0098	7	1.0447	33	1.0673	58	1.0744	83
1.0113	8	1.0459	34	1.0679	59	1.0742	84
1.0127	9	1 0470	35	1.0685	60	1.0739	85
1.0142	10	1.0481	36	1.0691	61	1.0736	86
1.0157	11	1 0492	37	1.0697	62	1.0731	87
1.0171	12	1.0502	38	1.0702	63	1.0726	88
1 0185	13	1.0513	39	1 0707	64	1.0720	89
1.0200	14	1.0523	40	1 0712	65	1.0713	90
1.0214	15	1.0533	41	1 0717	66	1.0705	91
1.0228	16	1.0543	42	1 0721	67	1.0696	92
1.0242	17	1.0552	43	1 0725	68	1.0686	93
1.0256	18	1 0562	44	1.0729	69	1.0674	94
1.0270	19	1.0571	45	1.0733	70	1.0660	95
1.0284	20	1.0580	46	1.0737	71	1.0644	96
1.0298	21	1.0589	47	1.0740	72	1.0625	97
1.0311	22	1.0598	48	1.0742	73	1.0604	98
1.0324	23	1.0607	49	1 0744	74	1.0580	99
1.0337	24	1.0615	50	1 0746	75	1.0553	100
1.0350	25						

DATA OF IMPORTANT INORGANIC COMPOUNDS

USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS[*]

Substance	Formula	Molecular or Atomic Weight	Weight of 1 milli-equivalent	Solubility in 100 g Water
Acetic acid	$HC_2H_3O_2$	60.05	0.06005	$69.87^{15°}$
Aluminum	Al	26.97	0.00899	
chloride	Al_2Cl_6	266.68	0.04445	40
chloride	$Al_2Cl_6 \cdot 12H_2O$	482.88	0.08048	
oxide	Al_2O_3	101.94	0.01699	insol.
sulfate	$Al_2(SO_4)_3$	342.12	0.05702	$36.1^{20°}$
sulfate	$Al_2(SO_4)_3 \cdot 18H_2O$	666.41	0.1111	87
Ammonia	NH_3	17.03	0.01703	
Ammonium	NH_4	18.04	0.01804	
chloride	NH_4Cl	53.50	0.05350	$29.4^{0°}$
hydroxide	NH_4OH	35.05	0.03505	
nitrate	NH_4NO_3	80.05	0.08005	$118^{0°}$
sulfate	$(NH_4)_2SO_4$	132.14	0.06607	$71^{5°}$
Antimony	Sb	121.76	0.06088	
Arsenic	As	74.91	0.03746	
oxide	As_2O_5	229.82	0.05746[*]	150
Arsenous oxide	As_2O_3	197.82	0.03297[†]	$1.74^{15°}$
Arsenous oxide	As_2O_3	197.82	0.04946[‡]	$1.74^{15°}$
Barium	Ba	137.36	0.06868	
carbonate	$BaCO_3$	197.37	0.09868	$.0022^{20°}$[5]
chloride	$BaCl_2$	208.27	0.1041	$30.9^{0°}$
chloride	$BaCl_2 \cdot 2H_2O$	244.31	0.1222	$36.2^{20°}$
hydroxide	$Ba(OH)_2$	171.38	0.08569	
hydroxide	$Ba(OH)_2 \cdot 8H_2O$	315.51	0.1577	$5.56^{15°}$
sulfate	$BaSO_4$	233.42	0.1167	$.000172^{0°}$
oxide	BaO	153.36	0.0768	$1.5^{0°}$
peroxide	BaO_2	169.36	0.08469	insol.
Bromine	Br	79.92	0.07992	$4.17^{15°}$
Cadmium carbonate	$CdCO_3$	172.42	0.08621	insol.
chloride	$CdCl_2$	183.32	0.09166	$140^{15°}$
chloride	$CdCl_2 \cdot 2.5H_2O$	228.36	0.1142	$168^{20°}$
sulfide	CdS	144.47	0.0723	insol.
Calcium	Ca	40.08	0.02004	.0013
carbonate	$CaCO_3$	100.09	0.05005	.0013
chloride	$CaCl_2$	110.99	0.055495	$59.5^{0°}$
chloride	$CaCl_2 \cdot 6H_2O$	219.086	0.10954	$117.4^{0°}$
hydroxide	$Ca(OH)_2$	74.10	0.03705	$.17^{5°}$
oxide	CaO	56.08	0.02804	$.13^{0°}$
sulfate	$CaSO_4$	136.14	0.06807	$.179^{0°}$
sulfide	CaS	72.14	0.03607	$.15^{10°}$
Carbon	C	12.010	0.006005[†]	insol.
dioxide	CO_2	44.01	0.02200[†]	$179.67 \text{ ml.}^{0°}$
Chlorine	Cl	35.46	0.03546[†]	$150 \text{ ml.}^{4°}$
Chromic anhydride	CrO_3	100.01	0.03334[†]	$163.4^{0°}$
oxide	Cr_2O_3	152.02	0.02534[†]	insol.
Citric acid	$H_3C_6H_5O_7$	192.12	0.06404	133.
Cobalt	Co	58.94	0.02947	
Copper	Cu	63.57	0.03178[4]	
oxide	CuO	79.57	0.07957[†]	
sulfate	$CuSO_4$	159.63	0.1596[†]	$20°$
sulfate	$CuSO_4 \cdot 5H_2O$	249.71	0.2497[†]	$31.61^{0°}$
sulfide	CuS	95.63	0.04781	.000033

[1] Precipitation reagents. [3] Acids and bases. [†] Oxidizing and reducing agents. [5] Reduction to Cu_2O.

[4] In the iodide method for determining copper the milliequivalent is 0.06357.

[*] Compiled and arranged by R. M. Meiklejohn.

USEFUL DATA OF THE MORE IMPORTANT INORGANIC
COMPOUNDS — *Continued*

Substance	Formula	Molecular or Atomic Weight	Weight of 1 milli-equivalent	Solubility in 100 g Water
Cyanogen.........	$(CN)_2$	52 02	0 02601	
		159.68	0 07984[2]	
		71.84	0 07184[2]	insol.
		151 91	0 1519[2]	
		278.01	0 2780[2]	32.8[0°]
		392.14	0 3921	18[0°]
		80 924	0 08093	221.2[0°]
		36 46	0.03646	82.5[10°]
		27 02	0 02702	
		20 01	0.02001	264
		127 93	0 1279	
		34 016	0 01701	
		34.076	0 01704	437 ml.[6°]
		126 92	0 1269	.0182[11°]
Iron..............	Fe	55.85	0 05585	
Lead.............	Pb	207 21	0 1036	
carbonate.......	$PbCO_3$	267 22	0.1336	.0019§
chromate.......	$PbCrO_4$	323.22	0.1616	.00002[18°]
		223 21	0 1116	
		239 21	0 1196	
		239 27	0 1196	.0001
		21 32	0 01216	
		84.33	0 04216	.0100
		95 23	0 04762	52.2[0°]
		203 33	0 1017	167
		40.32	0 02016	.00062
sulfate.........	$MgSO_4·7H_2O$	246 49	0 1232	26.9[0°]
Malic acid......	$H_2C_4H_4O_5$	134.09	0 06705	76.9[0°]
		54 93	0 02746	
		125 84	0 06292	62.16[18°]
		86 03	0 04346	insol.
		150 99	0 07549	53.2[0°]
		271 52	0 1358	5.73[0°]
		58 69	0 02934	
		63 02	0 06302[2]	
		63 02	0 02101[2]	
		76 02	0 01900[2]	
		108 02	0 05401[2]	
		108 02	0 01800[2]	
		47 02	0 04702	
		14 01	0 01401[2]	
		90 04	0 04502	
		126 07	0 06304	4.9[0°]
		98 00	0 09800[M]	v. sol.
		98 00	0 04900[P]	v. sol.
		98 00	0 03267[2]	v. sol.
		39 10	0 03910	
		100 11	0 1001	22.4[0°]
		188 18	0 1882	.37[0°]
		119 01	0 1190	53.48[0°]
		138 20	0 06910	80.4[0°]
carbonate.......	K_2CO_3			
chlorate........	$KClO_3$	122 56	0 02043[2]	3.3[0]4

[1] Precipitation reagents
M Methyl orange.   [2] Acids and bases
P. Phenolphthalein.   [3] Oxidizing and reducing agents.
Temp. C.

USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS — *Concluded*

Substance	Formula	Molecular- or atomic weight	Weight of 1 milli-equivalent	Solubility in 100 g Water[4]
Potassium chloride....	KCl	74.56	0.07456	28.5[o]
chromate..........	K_2CrO_4	194 20	0.06473[3]	61.5[oo]
chloroplatinate....	K_2PtCl_6	486.16	.....	insol. in alc.
cyanide..........	KCN	65.11	0.06511[5]	v. sol.
dichromate........	$K_2Cr_2O_7$	294.21	0.1471[3]	4.9[oo]
dichromate........	$K_2Cr_2O_7$	294 21	0.04903[3]	4.9[oo]
ferrocyanide......	$K_4Fe(CN)_6$	368.34[1]	0.3683[3]	
ferrocyanide......	$K_4Fe(CN)_6·3H_2O$	422 39[1]	0.4224	27.8[12o]
hydroxide.........	KOH	56.10	0.05610	107[15oo]
iodate............	KIO_3	214.01	0.03567	4.74[oo]
iodide............	KI	166.02	0.1660	126.1[oo]
nitrate...........	KNO_3	101.10	0.03370[1]	13 3[oo]
nitrite...........	KNO_2	85 10	0.08510[1]	300[15.5o]
oxide.............	K_2O	94 19	0.04710	v. sol.
permanganate......	$KMnO_4$	158.03	0.03161	2 83[oo]
sulfide...........	K_2S	110 25	0.05513	sol.
tartrate..........	$K_2H_2C_4O_6·½H_2O$	235.27	0.1176	sol.
thiocyanate.......	KCNS	97.17	0.09717	177.2[oo]
Silver............	Ag	107.88	0.1079	
nitrate...........	$AgNO_3$	169.89	0.1699	122[oo]
Sodium............	Na	23.00	0 02300	
bromide.........	NaBr	102.91	0.1029	79.5[oo]
bicarbonate.......	$NaHCO_3$	84.01	0.08402	6.90[oo]
carbonate.........	Na_2CO_3	106.00	0 05300	7.1[oo]
chloride..........	NaCl	58.45	0.05845	35.7[oo]
cyanide...........	NaCN	49 02	0.04902	sol.
hydroxide.........	NaOH	40.01	0.04001	133.3[12o]
iodide............	NaI	149 92	0.1499[1]	158.7[6o]
nitrate...........	$NaNO_3$	85.01	0.02834[1]	72.9[oo]
nitrite...........	$NaNO_2$	69 01	0.06901[1]	83.3[20o]
oxalate...........	$Na_2C_2O_4$	134.01	0.06700	3.22[1.25o]
oxide.............	Na_2O	61.99	0.03100	decomp.
phosphate (mono)...	$NaH_2PO_4·H_2O$	138.01[2]	0 1380(?)	v. sol.
phosphate (disod)...	Na_2HPO_4	141.98[2]	0.1420(?)	
phosphate (disod)...	$Na_2HPO_4·12H_2O$	358.17	0.3582(?)	6 3[oo]
phosphate (trisod)...	$Na_3PO_4·12H_2O$	380.16	0 3802	
sulfide...........	Na_2S	78.05	0.03903	15.4[10o]
thiosulfate.......	$Na_2S_2O_3·5H_2O$	248.20	0.2482	74.7[oo]
Stannous chloride...	$SnCl_2$	189.61	0.09481	83.9[oo]
chloride..........	$SnCl_2·2H_2O$	225.65	0.1128	118 7[oo]
oxide.............	SnO	134.70	0.06735	insol.
Sulfur dioxide....	SO_2	64 06	0.03203	7979 ml.[oo]
trioxide.........	SO_3	80.06	0 04003	
Sulfuric acid......	H_2SO_4	98.076	0 04904	
Tartaric acid.....	$H_2C_4H_4O_6$	150.09	0.07504	115[oo]
Tin...............	Sn	118 70	0.05935	
Zinc.............	Zn	65.38	0 03269	
carbonate.........	$ZnCO_3$	125.39	0.06269	.001[15o]
chloride..........	$ZnCl_2$	136.29	0.06814	209[oo]
oxide.............	ZnO	81.38	0 04069	.001[o]
sulfate...........	$ZnSO_4$	161.43	0 08071	43 02[oo]
sulfate...........	$ZnSO_4·7H_2O$	287.54	0.1438	115 2[oo]
sulfide...........	ZnS	97.44	0 04872	00069

[1] Precipitation reagents.   [2] Acids, bases and salts.   [3] Oxidizing and reducing agents.

[4] The small superior numbers in the last column refer to the temperature in degrees Centigrade.

[5] In the Liebig KCN titration and in the determination of nickel the milliequivalent is 0 1302.

COMPARISON OF METRIC AND CUSTOMARY UNITS (U.S.)

LENGTH

1 millimeter, mm = 0.03937 inch.	1 inch = 25 4 millimeters.
1 centimeter, cm = 0.39371 inch.	1 inch = 2 5400 centimeters.
1 meter, m = 3 2808 feet.	1 foot = 0.30480 meter.
1 meter = 1.0936 yards.	1 yard = 0.91440 meter.
1 kilometer = 0.62137 (U.S.) mile.	1 mile = 1.6094 kilometers.

AREAS

1 square millimeter, sq mm = 0.00155 sq in.	1 sq in = 645.16 sq mm.
1 square centimeter, sq cm = 0.1550 sq in.	1 sq in = 6.452 sq cm.
1 square meter, sq m = 10.764 sq ft.	1 sq ft = 0.0929 sq m.
1 square meter = 1.196 sq yd.	1 sq yd = 0.8361 sq m.
1 square kilometer = 0.3861 sq mi.	1 sq mi = 2.5900 sq km.
1 hectare = 2.471 acres.	1 acre = 0.4047 hectare.

VOLUMES

1 cubic millimeter, cu mm = 0.000061 cu in.	1 cu in = 16,387 cu mm.
1 cubic centimeter, ml = 0.06103 cu in.	1 cu in = 16.387 ml.
1 cubic meter = 35.314 cu ft.	1 cu ft = 0 02832 cu m.
= 61,028 cu in	= 28.32 liters.
1 cubic meter = 1.3079 cu yd.	1 cu yd = 0.7645 cu m.

CAPACITIES

1 cubic centimeter, ml = 0.03381 (U.S.) liquid oz.	1 ounce = 29.574 ml.
1 cubic centimeter = 0.2705 (U.S.) apothecaries' dram.	1 dram = 3.6967 ml.
1 cubic centimeter = 0.8115 (U.S.) apothecaries' scruple	1 scruple = 1.2322 ml.
1 liter = 1.05668 (U.S.) liquid qt.	1 quart = 0.94636 liter.
1 liter = 0.26417 (U.S.) gallon.	1 gallon = 3.78543 liters.
1 liter = 0.11351 (U.S.) peck.	1 peck = 8.80982 liters.
1 hectoliter = 2.83774 (U.S.) bushels.	1 bushel = 0.35239 hectoliter.

MASSES

1 gram = 15.432 grains.	1 grain = 0 06480 gram.
1 gram = 0 03527 avoirdupois ounce.	
	1 ounce (av.) = 28 350 grams = 437.5 grains.
1 gram = 0.03215 troy ounce.	1 ounce (troy) = 31.103 grams = 480 grains.
1 kilogram = 2.2046 pounds (av.).	1 pound (av.) = 0.4536 kilogram.
1 kilogram = 2.6792 pounds (troy).	1 pound (troy) = 0.37324 kilogram.

WEIGHTS, VOLUMES, ETC.

AVOIRDUPOIS WEIGHT

The system of weights in ordinary use by which common or heavy articles are weighed.

16 drams	= 1 ounce	= 28.35 grams.
16 ounces	= 1 pound	= 453.59 grams.
25 pounds	= 1 quarter	= 11.34 kilograms.
4 quarters	= 1 hundred weight	= 45.359 kilograms.

APOTHECARIES' WEIGHT (and TROY)

The system of weights sometimes employed in weighing medicines (and precious metals).

1 grain		= 0.0648 gram.
20 grains	= 1 scruple	= 1.296 grams.
3 scruples	= 1 drachm	= 3.888 grams.
8 drachms	= 1 ounce	= 31.10 grams.
12 ounces	= 1 pound	= 373.23 grams.

1 apothecaries' (or troy) pound contains 5760 grains.
1 apothecaries' (or troy) ounce contains 480 grains.
1 troy pound = 12 troy ounces = 13.166 avoirdupois ounces = 240 pennyweights.

FLUID MEASURE

1 minim		= 0.06161 cubic centimeter.
60 minims	= 1 fluid drachm	= 3.696 cubic centimeters.
8 fluid drachms	= 1 fluid ounce	= 29.573 cubic centimeters.
16 fluid ounces	= 1 U.S. pint	= 473.18 cubic centimeters.
8 pints	= 1 U.S. gallon	= 3.785 liters.

1 U.S. gallon contains 231 cubic inches.

The minim, fluid drachm, fluid ounce and pint are the fluid measures sometimes employed by apothecaries.

1 U.S. gallon of water = 8.64 lbs.

Useful Approximations

1 molecular weight in grams of a gas = 22.4 liters.
1 molecular weight in pounds of a gas = 359 cubic feet.

To find temperatures on the absolute scales, which starts at the "absolute" zero, add 273° to the reading of the Centigrade thermometer or 459.4° to the reading of the Fahrenheit thermometer. The so-called "standard conditions" for measuring gases (0° and 760 mm of Hg pressure) are 273° (absolute) and 760 mm or 491.4° F. (absolute) and 29.92 inches of mercury pressure or 14.7 pounds per square inch.

SPECIFIC GRAVITIES OF COMMON SUBSTANCES

Aluminum	2.7	Lead	11.3	Quartz	2.66
Brass	8.4	Marble	2.7	Rock Salt	2.15
Cast iron	7.3	Mercury	13.6	Silver	10.5
Glass	2.6	Nickel	8.7	Steel	7.8
Gold	19.3	Platinum	21.4	Sulfur	2.05
Ivory	1.9	Porcelain	2.4	Zinc	7.10

TABLES FOR CALCULATING ANALYSES

DIRECTIONS FOR USING THE TABLES

Computations of Gravimetric Analysis. The methods of computing the results in gravimetric work have been shown in the text. In the so-called *direct analysis* it is assumed that all the desired element in the original substance is converted into a weighed precipitate of which a known fraction consists of the element in question. The fraction, usually expressed as a decimal, which represents the amount of an element A in one of its compounds is commonly called the *chemical factor*: It represents the weight of A in 1 part by weight of the compound, independent of what unit of weight is used.

Thus, to be specific, 1 g of silver chloride contains 0.7526 g of silver; 1 lb of silver chloride contains 0.7526 lb of silver. If p g of silver chloride is obtained from s g of original substance, then $0.7526 p$ is the weight of silver in the sample taken and $\dfrac{0.7526\, p \times 100}{s}$ = per cent of silver in the substance analyzed. The general rule for computing a direct gravimetric analysis is as follows: Multiply the weight of the precipitate by 100 times the chemical factor and divide by the weight of the original substance. Using the notation as above:

$$\frac{p \times \text{chem. factor} \times 100}{s} = \text{desired percentage}$$

A table of chemical factors is given on the following pages. The use of the table may be illustrated by an example:

From 0.5 g of arsenic ore, 0.4761 g of $Mg_2As_2O_7$ was obtained. What is the percentage of arsenic in the ore?

In the table (p 768) we seek " As " under the heading " Sought " and $Mg_2As_2O_7$ under the heading " Found," and we find on the same line that the chemical factor is 0.4820. Finally, in the fourth column we find that the logarithm of this number multiplied by 100 is 1.6830. The computation is as follows:

log factor × 100	1.6830
log 0.4761	9.6777 − 10
colog 0.5	0.3010
	1.6623 log of 45.95

The ore contains 45.95 per cent of arsenic.

If the weight of ore had been 0.4826 g (a so-called *factor* weight) the percentage of arsenic would have been found by multiplying the weight of precipitate by 100.

This table of factors is convenient, but every chemist should know how to compute any factor. As this often causes trouble for beginners, the method of computing the factors will be discussed.

Computing the Factor. The symbol AgCl shows that 1 atomic weight of silver, 107.88, is present in 1 molecular weight of silver chloride, 143.34. This ratio of weights is independent of the unit of weight used and is just as true of tons, pounds, ounces, or grains as it is of grams. Using the conception of the gram-molecular weight, the formula shows that 107.88 g of silver is present in 143.34 g of silver chloride. If 143.34 g of silver chloride contains 107.88 g of silver, 1 g of silver chloride will contain $\dfrac{107.88}{143.34} = 0.7526$ g silver. In other words, the chemical

factor for silver in silver chloride is found by dividing the atomic weight of silver by the molecular weight of silver chloride. Using symbols, the chemical factor in this case is $\dfrac{Ag}{AgCl}$. It represents the ratio of *what is sought* to *what is found.*

In the arsenic analysis referred to above, the symbol for magnesium pyroarsenate, $Mg_2As_2O_7$, shows that 2 atoms of arsenic are present in the molecule. The chemical factor is $\dfrac{2As}{Mg_2As_2O_7} = \dfrac{149.8}{310.6} = 0.4826.$

As a still more complicated case, assume that a sample of magnetite is analyzed in such a way that all the iron is converted into Fe_2O_3 and it is desired to know the weight of Fe_3O_4 originally present. The chemical factor for converting a weight of Fe_2O_3 into the equivalent weight of Fe_3O_4 is

The concept of the *chemical factor* may be applied to any precipitate. The following equation represents the reaction between ferrous ions and dichromate ions:

$$6Fe^{++} + Cr_2O_7^{--} + 14H^+ \rightarrow 6Fe^{+++} + 2Cr^{+++} + 7H_2O$$
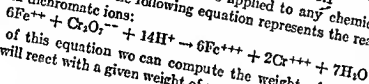
On the basis of this equation we can compute the weight of ferrous ammonium sulfate which will react with a given weight of potassium dichromate. The chemical factor is

$$\frac{6[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]}{K_2Cr_2O_7} = \frac{6 \times 392.1}{294.2} = 7.997.$$

If the weight of dichromate is multiplied by this factor the product will be the equivalent of ferrous ammonium sulfate. If a weight of ferrous ammonium sulfate is divided by 7.997, the quotient is the equivalent weight of dichromate.

It is possible to arrive at the same result by a slightly different method of reasoning, and this other method is more like the one used in volumetric computations. If the weight of ferrous ammonium sulfate, p, is divided by the molecular weight of ferrous ammonium sulfate, the quotient represents the number of moles of ferrous ammonium sulfate present. The equation, however, shows that one-sixth as many moles of dichromate are required so that by dividing by 6 and multiplying by the molecular weight of dichromate the weight of dichromate is obtained. In each case the computation may be expressed as follows:

$$\frac{p \times K_2Cr_2O_7}{FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \times 6} = \text{weight of dichromate}$$

The fraction $\dfrac{K_2Cr_2O_7}{6FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O}$ represents the weight of dichromate which corresponds to 1 g of ferrous ammonium sulfate; the fraction

$$\frac{p}{FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O}$$

represents the number of moles of ferrous ammonium sulfate present.

It is evident from the foregoing discussion that ordinary chemical arithmetic is really very simple. Formerly the so-called "rule of three" was used more in elementary textbooks on arithmetic than it is today. Most textbooks on analytical chemistry have been taught to use proportions in chemical arithmetic instead of reasoning out unit values as more than in the United States. In Germany it is still used influenced by German practice and beginners in chemistry have been taught to they have been taught before studying chemistry. In the above discussion not

a single proportion has been written out to be solved mechanically by the rule that "the product of the means is equal to the product of the extremes."

Computations of Volumetric Analysis.

1. *Relative Strength of Solutions.*

(a) If a ml of solution $A = b$ ml of solution B, then

$$1 \text{ ml of solution } A = \frac{b}{a} \text{ ml solution } B; \quad 1 \text{ ml of } B = \frac{a}{b} \text{ ml of } A.$$

(b) If solution A is N-normal, then solution B is $\frac{a}{b} \times N$-normal.

(c) If solution A is N-normal and solution B is M-normal, then 1 ml of $A = N/M$ ml of B, 1 ml of $B = M/N$ ml of A.

2. *Normal Strength or Normality.*

The *normal strength* gives the number of milliequivalents contained in 1 ml of solution. Thus, 1 ml of a normal solution contains 1 milliequivalent in each milliliter.

(a) To find the normality, divide the value of 1 ml in terms of any pure substance by the milliequivalent of that substance. Thus, if ml represents the milliliters of solution that contains or is equivalent to g g of a pure substance (of which the milliequivalent is e), then the normality, N, is $\frac{ml \times e}{g} = N$.

(b) If N is the normality, and e the milliequivalent, then 1 ml of the solution $= e \times N$ g of the substance in question.
The milliequivalent may be part of the molecule: thus
1 ml of 0.3 N acid $= 0.3 \times 0.031$ g of Na_2O.

3. *General Method of Finding the Percentage by Weight.*

Let ml represent the net volume of reagent required, N the normality of the reagent, s the weight of substance taken, and e the milliequivalent weight of the constituent whose percentage is required.

Then $\dfrac{ml \times N \times e \times 100}{s}$ = per cent.

Note that, if $s = N \cdot e \cdot 100$, then ml = per cent.

4. *Equivalent Weights*

(a) Acids. Let M = molecular weight, MO = methyl orange, P = phenolphthalein. The first three acids may be titrated with either indicator.

Acid	Equivalent
HCl	M
HNO₃	M
H₂SO₄	M/2
HC₂H₃O₂	M (With P)
H₂C₄H₄O₆	M/2 (With P)
H₂CO₃	M (With P)
KHC₄H₄O₆	M (With P)
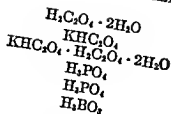
$H_2C_2O_4 \cdot 2H_2O$	$M/2$ (With P)
KHC_2O_4	M (With P)
$KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$	$M/3$ (With P)
H_3PO_4	M (With MO)
H_3PO_4	$M/2$ (With P)
H_3BO_3	M (With P and glycerol, not acid to MO)

(b)

Bases	Equivalent
KOH	M
NaOH	M
NH_4OH	M (With MO)
$Ba(OH)_2$	$M/2$

(c) SALTS OF WEAK ACIDS

Salts of carbonic and boric acids may be titrated with methyl orange as if the free base were present. With phenolphthalein the end point is reached when the carbonate is completely changed to bicarbonate. Thus Na_2CO_3 titrates as if it were $2NaOH$ with methyl orange but reacts with only one (1) equivalent of acid if phenolphthalein is used in the cold.

(d) OXIDIZING AGENTS:
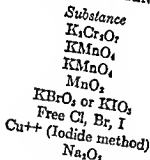
Substance	Reduction Change	Equivalent
$K_2Cr_2O_7$	Each Cr loses 3 charges	$M/6$
$KMnO_4$	Mn^{+vii} to Mn^{+ii}	$M/5$
$KMnO_4$	Mn^{+vii} to MnO_2	$M/3$
MnO_2	Mn^{+iv} to Mn^{+ii}	$M/2$
$KBrO_3$ or KIO_3	(Br or I)$^{+v}$ to (Br or I)$^{-i}$	$M/6$
Free Cl, Br, I	To (Cl, Br, or I)$^{-i}$	At. Wt.
Cu^{++} (Iodide method)	To Cu^+	At. Wt.
Na_2O_2	$O^\pm$ to O^-	$M/2$

(e) REDUCING AGENTS:
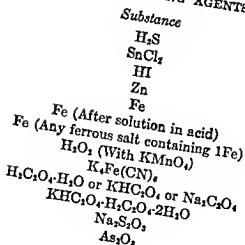
Substance	Oxidation Change	Equivalent
H_2S	S^- to S^0	$M/2$
$SnCl_2$	Sn^{++} to Sn^{+++}	$M/2$
HI	I^- to I^0	M
Zn	Zn^0 to Zn^{++}	$M/2$
Fe	Fe^0 to Fe^{++}	At. Wt.
Fe (Any ferrous salt containing 1Fe)	Fe^{++} to Fe^{+++}	At. Wt.
H_2O_2 (With $KMnO_4$)	$O^\pm$ to O^{++}	M
$K_4Fe(CN)_6$	To $[Fe(CN)_6]^=$	$M/2$
$H_2C_2O_4 \cdot H_2O$ or KHC_2O_4 or $Na_2C_2O_4$	To $2CO_2$	M
$KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$	To $4CO_2$	$M/2$
$Na_2S_2O_3$	To $\frac{1}{2}Na_2S_4O_6$	$M/4$
As_2O_3	To $2AsO_2^-$ or $2AsO_3^-$	M $M/4$

5. *Equivalent weight depends on the reaction.*

Considered as a salt (that is, as if it were a precipitant) the equivalent weight of $KMnO_4 = M$. A solution of $KMnO_4$ which is normal as a salt would be $5\,N$ in a reaction with a ferrous salt whereby the Mn loses 5 valence charges, and would be $3\,N$ in a reaction whereby the $KMnO_4$ is only reduced to MnO_2.

Similarly the equivalent weight of potassium binoxalate, KHC_2O_4, or of potassium tetroxalate, $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$, depends upon the replaceable hydrogen when considered as an acid, but as reducing agents the oxalate content alone is to be considered. A solution of tetroxalate which is normal as an acid is four-thirds normal as a reducing agent. Arsenic acid is like phosphoric acid as an acid, but in the reaction with hydriodic acid the As is reduced from the quinquevalent to the trivalent state (cf. pp. 448–452).

In the following tables the values of the chemical factors are given to four significant figures and with four-place logarithms. Most chemical work is not sufficiently precise to justify the use of five- or six-place logarithms, and the four-place table is much easier to use. In some handbooks, if not in all, the molecular weights are given to as many significant figures as is possible from the international atomic weights. This involves two erroneous assumptions, namely, that the atomic weights are known positively to the last decimal given in the atomic-weight table and that the gram-molecular weight, with weighings made in the air with brass weights, is the exact sum of the atomic weights on a vacuum basis. The analytical chemist rarely allows for air displacement by the weights and objects weighed, but this is done in atomic-weight determinations. Thus, according to the atomic-weight table, the molecular weight of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ is 392.146, but the value is really 391.890 on the basis of air weighing. The value 392 1 as obtained from the table to four significant figures does not lead to the erroneous assumption that the value is known to more than the first decimal. Moreover, although hydrogen may be known to the third decimal place, the value of iron is doubtful in the second decimal place, and the accuracy of the molecular weight of an iron compound is doubtful in the second decimal place at best.

CHEMICAL FACTORS

CHEMICAL FACTORS* (CALCULATED FOR 1941)

Sought	Found	Factor	Log
Ag	$AgBr$	0.5744	9.7593
	$AgCl$	0.7526	9.8766
	$AgCN$	0.8057	9.9062
	AgI	0.4595	9.6622
	$AgNO_3$	0.6350	9.8028
	Ag_2O	0.9310	9.9689
	Ag_2S	0.8706	9.9398
	Ag_3PO_4	0.7731	9.8882
	$Ag_4P_2O_7$	0.7127	9.8529
Ag_2O	$AgCl$	0.8084	9.9076
Al	Al_2O_3	0.5291	9.7236
	$AlPO_4$	0.2212	9.3447
Al_2O_3	$AlPO_4$	0.4178	9.6210
AlF_3	CaF_2	0.7170	9.8555
$AlCl_3$	Al_2O_3	2.610	9.4177
$Al_2(SO_4)_3$	Al_2O_3	3.356	9.5258
$Al_2(SO_4)_3,18H_2O$	Al_2O_3	6.537	0.8154
As	As_2O_3	0.7574	9.8793
	As_2O_5	0.6519	9.8142
	As_2S_3	0.6090	9.7846
	As_2S_5	0.4831	9.6840
	I_2	0.2951	9.4700
	$Mg_2As_2O_7$	0.4826	9.6836
	$Mg_2P_2O_7$	0.6730	9.8280
	$(NH_4MgAsO_4)_2 \cdot H_2O$	0.3937	9.5952
As_2O_3	As_2O_5	0.8608	9.9349
	As_2S_3	0.8041	9.9054
	As_2S_5	0.6379	9.8047
	$2I_2$	0.3897	9.5907
	$Mg_2As_2O_7$	0.6372	9.8043
	$Mg_2P_2O_7$	0.8887	9.9487
	$(NH_4MgAsO_4)_2 \cdot H_2O$	0.5198	9.7159
AsO_3	As_2S_3	0.9993	9.9997
	As_2S_5	0.7927	9.8991
	$Mg_2As_2O_7$	0.7918	9.8986
	$Mg_2P_2O_7$	1.104	0.0431
	$(NH_4MgAsO_4)_2 \cdot H_2O$	0.6159	9.8102
As_2O_5	As_2S_3	0.9342	9.9705
	As_2S_5	0.7411	9.8699
	$2I_2$	0.4527	9.6558
	$Mg_2As_2O_7$	0.7403	9.8694
	$Mg_2P_2O_7$	1.032	0.0139
	$(NH_4MgAsO_4)_2 \cdot H_2O$	0.6039	9.7810
AsO_4	As_2S_3	1.129	0.0528
	As_2S_5	0.8957	9.9522
	I_2	0.5473	9.7382
	$Mg_2As_2O_7$	0.8949	9.9518
	$Mg_2P_2O_7$	1.2477	0.0962
	$(NH_4MgAsO_4)_2 \cdot H_2O$	0.7300	9.8633
Au	$AuCl_3$	0.6496	9.8126
	$HAuCl_4.4H_2O$	0.4785	9.6799
	$KAu(CN)_4.H_2O$	0.5503	9.7406
B	B_2O_3	0.3107	9.4924
	KBF_4	0.08593	8.9342
	H_3BO_3	0.1750	9.2430
	$Na_2B_4O_7.10H_2O$	0.1135	9.0549
B_2O_3	KBF_4	0.2766	9.4418
	H_3BO_3	0.5630	9.7505
	$Na_2B_4O_7.10H_2O$	0.3652	9.5625
BO_2	B_2O_3	1.230	0.0898
BO_3	B_2O_3	1.689	0.2277
B_4O_7	B_2O_3	1.115	0.0472
Ba	$BaCl_2.2H_2O$	0.5621	9.7498
	$BaCO_3$	0.6960	9.8426
	$BaCrO_4$	0.5421	9.7341
	$BaSO_4$	0.5885	9.7697
	$BaSiF_6$	0.4916	9.6916
BaO	$BaCO_3$	0.7770	9.8904
	$BaCrO_4$	0.6053	9.7820
	$BaSO_4$	0.6570	9.8176
	$BaSiF_6$	0.5489	9.7395

* The use of the table will be illustrated by two examples. (1) What weight of silver corresponds to p grams of silver bromide? Look up Ag in the column "Sought" and AgBr in the column "Found." For computation with a slide rule, use column 3, $p \times 0.5744$ = weight of Ag. (2) What weight of silver bromide corresponds to q grams of silver? With logarithms, log p + 9.7592 = log weight of Ag. Use the same factor as before but divide by it or subtract the logarithm.

Strictly speaking, the logarithm in the above case is not 9.7592 but 9.7592 − 10 or $\bar{1}.7592$, in which the characteristic is a negative number and the mantissa a positive fraction. It is a little easier to use the first expression and in chemical computations it is not necessary to write out the − 10 each time because there is never any doubt whether the computation is 7, 8, or 9 instead of a very large number or a number less than unity.

In computing the weight of silver bromide it represents a ... add the co-logarithm 0.2407 which is obtained quickly by subtracting each digit of 9.7592 from 9 except the last one which is subtracted from 10. It gives the logarithm of $\dfrac{1}{0.5744} = 0.2408$.

CHEMICAL FACTORS — Continued

Sought	Found	Factor	Log	Sought	Found	Factor	Log
BaO₂	Ba	1.233	0.0909	CO₂	MgCO₃	0.5219	9.7176
	BaCrO₄	0.6685	9.8251		Mg(HCO₃)₂	0 6014	9.7791
	BaSO₄	0.7256	9.8607		MgO	1.091	0.0379
B..CO	D..SO.	0.8456	0.0071		MnCO₃	0.3829	9 5330
					Mn(HCO₃)₂	0.4974	9 6967
					Na₂CO₃	0.4151	9.6182
					NaHCO₃	0.5238	9.7192
					Na₂O	0.7099	9.8512
Be	BeO	0.3605	9 5569		(NH₄)₂CO₃	0.4550	9.6608
BeO	BeCl₂	0.3130	9.4956		PbCO₃	0.1647	9.2166
BeO	BeSO₄.4H₂O	0.1412	9.1500		Rb₂CO₃	0.1905	9.2800
					Rb(HCO₃)	0.3004	9.4777
Bi	Bi₂O₃	0.8970	9 9528		SrCO₃	0 2980	9.4743
	BiOCl	0.8024	9.9044		Sr(HCO₃)₂	0 4198	9 6230
	BiPO₄	0.6874	9.8372		SrO	0.4247	0 6281
	Bi₂S₃	0.8129	9.9101		ZnCO₃	0.3509	9.5452
	BiAsO₄	0.6006	9.7786				
Bi₂O₃	Bi	1.115	0.0472	CO₂	CO₂	1.364	0.1347
	BiOCl	0.8946	9.9516	Ca	CaCl₂	0.3611	9.5576
	BiPO₄	0.7663	9 8844		CaCO₃	0.4005	9 6025
	Bi₂S₃	0.9063	9 9573		CaC₂O₄.H₂O	0.2743	9.4382
	BiAsO₄	0.6696	9 8258		CaC₂O₄	0.3129	9.4954
	BiONO₂	0.8118	9.9095		CaF₂	0.5133	9 7103
	Bi(NO₃)₃.5H₂O	0.4803	9.6815		CaO	0.7146	9 8541
					CaSO₄	0.2944	9.4659
Br	Ag	0.7408	9.8697		CO₂	0.9109	9.9595
	AgBr	0.4256	9.6290	CaO	CaCO₃	0.5603	9.7484
	AgCl	0.5576	9.7463		CaC₂O₄.H₂O	0.3838	9.5841
	HBr	0.9874	9.9945		CaC₂O₄	0.4378	9 6413
BrO₃	Ag	1.186	0.0740		CaF₂	0.7182	9 8563
	AgBr	0.6812	9.8332		Ca(HCO₃)₂	0 3459	9 5390
Br₂O₅	Ag	1 111	0 0459		Ca(H₂PO₄)₂.H₂O	0.2225	9 3472
	AgBr	0.6386	9 8052		Ca₂P₂O₇	0.4414	9.6448
C	CO₂	0.2729	9.4360		Ca(HSO₃)₂	0.2773	9.4430
	BaCO₃	0 0609	8 7843		Ca₃(PO₄)₂	0.5424	9.7343
CO₂	BaCO₃	0 2230	9.3483		CaSO₄	0.4667	9 6691
	BaO	0.2870	9.4578		CaSO₄	0.4119	9.6148
	Ba(HCO₃)₂	0.3393	9 5308		CaSO₄.2H₂O	0.3257	9.5128
	CaCO₃	0.4397	9.6434		CO₂	1.274	9.1053
	Ca(HCO₃)₂	0.5429	9.7348	Ca₃(PO₄)₂	Mg₂P₂O₇	1.394	0.1441
	CaO	0.7846	9.8946	CaS	BaS	0.3091	9 4001
	CO₃	0.7334	9.8653	CaSO₄	BaSO₄	0 5832	9.7658
	Cs₂CO₃	0.1351	9 1306	CaSO₄.2H₂O	CaO	3 070	0.4872
	FeCO₃	0.3799	9.5797	CaF₂	CaSO₄	0 5735	9.7586
	Fe(HCO₃)₂	0.4948	9 6944	Cb	Cb₂O₅	0.6990	9 8445
	K₂CO₃	0.3184	9.5029	Cd	CdO	0.8754	9.9422
	KHCO₃	0.4396	9 6431		CdS	0.7781	9.8910
	Li₂CO₃	0 5956	9.7750		CdSO₄	0 5392	9.7317
	LiHCO₃	0.6476	9.8112	CdO	CdS	0.8888	9.9488
					Cd	1.142	0.0578
					CdSO₄	0.6160	9.7896

CHEMICAL FACTORS — Continued

Sought	Found	Factor	Log	Sought	Found	Factor	Log
CdS	Cd...............	1.285	0.1090	Cr	PbCrO₄.......	0.1609	9.2067
	CdO.............	1.125	0.0512		K₂Cr₂O₇......	0.3535	9.5484
	CdSO₄..........	0.6930	9.8407		K₂CrO₄.......	0.2678	9.4278
Ce	Ce(NO₃)₄.......	0.3610	9.5575	Cr₂O₃	BaCrO₄.......	0.3000	9.4771
	Ce₂O₃..........	0.8538	9.9313		PbCrO₄.......	0.2352	9.3715
	CeO₂...........	0.8141	9.9107		CrO₃.........	0.7600	9.8808
	Ce₂(SO₄)₃......	0.4930	9.6929	CrO₂	BaCrO₄.......	0.3947	9.5963
Ce₂O₃	CeO₂...........	0.9536	9.9794		Cr₂O₃........	1.316	0.1192
Cl	Ag.............	0.3287	9.5168		PbCrO₄.......	0.3094	9.4906
	AgCl...........	0.2474	9.3933		K₂CrO₄.......	0.5150	9.7118
	AgNO₃..........	0.2087	9.3196		K₂Cr₂O₇......	0.6799	9.8324
	HCl............	0.9724	9.9878	CrO₄	BaCrO₄.......	0.4578	9.6607
	I..............	0.2794	9.4462		Cr₂O₃........	1.526	0.1837
	KCl............	0.4756	9.6772		PbCrO₄.......	0.3589	9.5550
	MnO₂...........	0.8158	9.9116	Cs	CsCl.........	0.7893	8.8973
	NaCl...........	0.6066	9.7829		Cs₂O.........	0.9432	9.9740
	NH₄Cl..........	0.6628	9.8214		Cs₂CO₃.......	0.8157	9.9116
	RbCl...........	0.2932	9.4672		Cs₂SO₄.......	0.7344	8.8659
ClO₃	AgCl...........	0.5823	9.7651		Cs₂PtCl₆.....	0.3945	9.5960
	KCl............	1.119	0.0490	Cs₂O	CsCl.........	0.8370	9.9227
	NaCl...........	1.428	0.1546		Cs₂CO₃.......	0.8650	9.9370
ClO₄	AgCl...........	0.6939	9.8413		Cs₂SO₄.......	0.7788	9.8914
	KCl............	1.334	0.1251		Cs₂PtCl₆.....	0.4182	9.6214
	NaCl...........	1.701	0.2308	Cu	Cu₂O.........	0.8882	9.9485
CN	AgCN...........	0.1943	9.2886		CuO..........	0.7989	9.9025
	Ag.............	0.2413	9.3826		Cu₂S.........	0.7986	9.9023
	KCN............	0.3996	9.6016		Cu₂(CNS)₂....	0.5226	9.7181
	NaCN...........	0.5308	9.7249		CuSO₄........	0.3982	9.6001
	HCN............	0.9627	9.9835		CuSO₄.6H₂O...	0.2546	9.4058
CNS	AgCNS..........	0.3500	9.5440	CuO	Cu...........	1.252	0.0975
	Cu₂(CNS)₂......	0.4774	9.0789		Cu₂O........	1.112	0.0460
	BaSO₄..........	0.2488	9.3959		Cu₂S........	0.9996	9.9998
	KCNS...........	0.5977	9.7765		Cu₂(CNS)₂....	0.6541	9.8156
	NH₄CNS.........	0.7630	9.8825		CuSO₄........	0.4985	9.6976
Co	Co(NO₃)₂.6H₂O..	0.2025	9.3064		CuSO₄.5H₂O...	0.3186	9.5082
	K₃Co(NO₂)₆.....	0.1303	9.1150	Er₂O₃	Er...........	1.144	0.0583
	CoO............	0.7865	8.8957	Er	Er₂O₃........	0.8745	9.9417
	Co₃O₄..........	0.7342	9.8658	F	BaSiF₆.......	0.4080	9.6107
	CoSO₄..........	0.3803	9.5801		CaF₂.........	0.4866	9.6872
	CoSO₄.7H₂O.....	0.2097	9.3216		CaSO₄........	0.2791	9.4457
CoO	Co.............	1.271	0.1043		HF...........	0.9500	9.9777
	Co(NO₃)₂.6H₂O..	0.2575	9.4107		H₂SiF₆.......	0.7913	9.8983
	K₃Co(NO₂)₆.....	0.1657	9.2193		K₂SiF₆.......	0.5176	9.7140
	Co₃O₄..........	0.9336	9.9702		NaF..........	0.4524	9.6555
	CoSO₄..........	0.4835	9.6844		SiF₄.........	0.7302	9.8634
	CoSO₄.7H₂O.....	0.2666	9.4258	Fe	Fe₂O₃........	0.6994	9.8447
Cr	BaCrO₄.........	0.2052	9.3125		FeCl₂........	0.4405	9.6440
	Cr₂O₃..........	0.6842	9.8352		FeCl₃.6H₂O...	0.2066	9.3152

CHEMICAL FACTORS — Continued

Sought	Found	Factor	Log
Fe	Fe(HCO₃)₃	0.3140	9.4969
	FeO	0.7773	9.8906
	Fe₃O₄	0.7236	9.8595
	FePO₄	0.3702	9.5684
	FeS	0.6352	9.8029
	FeSO₄	0.3676	9.5654
	FeSO₄.7H₂O	0.2009	9.3029
	FeSO₄(NH₄)₂ SO₄.6H₂O	0.1424	9.1536
FeO	Fe	1.287	0.1094
	FeCO₃	0.6202	9.7925
	Fe(HCO₃)₃	0.4039	9.6063
	Fe₃O₄	0.8998	9.9542
	FePO₄	0.4761	9.6777
	FeS	0.8172	9.9123
	FeSO₄	0.4729	9.6747
	FeSO₄.7H₂O	0.2584	9.4123
	FeSO₄(NH₄)₂ SO₄.6H₂O	0.1832	9.2630
Fe₂O₃	Fe	1.430	0.1553
	FeCl₃	0.4922	9.6922
	FeCO₃	0.6892	9.8383
	Fe₃O₄	1.035	0.0149
	FePO₄	0.5292	9.7237
	FeS	0.9082	9.9582
	FeS₂	0.6655	9.8231
	Fe₂(SO₄)₃	0.3993	9.6013
	(NH₄)₂SO₄.Fe₂ (SO₄)₃.24H₂O	0.1656	9.2190
FeS₂	BaSO₄	0.2570	9.4099
H	H₂O	0.1119	9.0488
H₃BO₃	B₂O₃	1.776	0.2495
HBr	Ag	0.7501	9.8751
	AgBr	0.4309	9.6344
HCl	Ag	0.3380	9.5290
	AgCl	0.2544	9.4056
	CaCO₃	0.7286	9.8625
	KCl	0.4891	9.6891
	K₂O	0.7743	9.8889
	NaCl	0.6239	9.7951
	Na₂O	1.176	0.0705
	NH₄Cl	0.6817	9.8335
	SnCl₂	0.5600	9.7480
	Na₂CO₃ methyl orange	0.6880	9.8376
	Na₂C₂O₄ standardization	0.5412	9.7358
HF	BaSiF₆	0.4296	9.6331
	CaF₂	0.5126	9.7098
	CaSO₄	0.2939	9.4682

Sought	Found	Factor	Log
HF	F	1.053	0.0224
	K₂SiF₆	0.5451	9.7364
HI	Ag	1.186	0.0740
	AgI	0.5448	9.7362
	Pd	2.398	0.3799
	PdI₂	0.7097	9.8510
HNO₂	AgNO₂	0.3055	9.4850
	NO	1.567	0.1950
HNO₃	KNO₃	0.6233	9.7947
	N	4.498	0.6530
	NaNO₃	0.7413	9.8700
	NH₃	3.701	0.5683
	NH₄Cl	1.178	0.0711
	(NH₄)₂PtCl₆	0.2838	9.4530
	NO	2.100	0.3222
	N₂O₃	1.658	0.2196
	N₂O₅	1.370	0.1367
	N₂O₄	1.107	0.0971
	C₂₀H₁₅N₃HNO₃	0.1079	9.9250
	Pt	0.6457	9.8100
H₃PO₄	HPO₃	1.225	0.0881
	H₄P₂O₇	1.101	0.0419
	Mg₂P₂O₇	0.8806	9.9448
	P	3.163	0.5001
	P₂O₅	1.380	0.1401
H₃PtCl₆.6H₂O	Pt	2.654	0.4239
H₂S	BaSO₄	0.1460	9.1644
	CdS	0.2359	9.3727
	FeS	0.3877	9.5885
	S	1.063	0.0265
H₂SeO₃	Se	1.633	0.2131
H₂SiF₆	BaSiF₆	0.5157	9.7124
	3CaF₂	0.6151	9.7889
	F	1.264	0.1018
	2HF	3.601	0.5564
	6HF	1.200	0.0792
	K₂SiF₆	0.6541	9.8157
	SiF₄	1.384	0.1412
H₂SO₃	Al₂(SO₄)₃	0.8601	9.9345
	Ba(OH)₂	0.5723	9.7576
	BaSO₄	0.4200	9.6232
	K₂Al₂(SO₄)₄. 24H₂O	0.4135	9.6165
	K₂O	1.011	0.0176
	KOH	0.8742	9.9416
	K₂SO₄	0.5629	9.7501
	Na₂CO₃	0.9252	9.9662
	Na₂C₂O₄	0.7319	9.8641

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log	Sought	Found	Factor	Log
H_2SO_4	$(NH_4)_2SO_4$	0.7422	9.8705	$KClO_3$	$AgCl$	0.8550	9.9320
Hg	Hg_2Cl_2	0.8498	9.9293		KCl	1.6438	0 2158
	$HgCl_2$	0.7388	9.8686	$KClO_4$	$AgCl$	0.9667	9.9853
	HgO	0.9261	9.9666		KCl	1.858	0.2691
	HgS	0.8622	9.9356	KCN	$AgCN$	0.4863	9.6869
$HCNS$	$AgCNS$	0.3560	9.5515		$AgNO_3$ (Liebig method)	0.7665	9.8845
	$Cu_2(CNS)_2$	0.4857	9.6864		$AgCl$	0.4542	9.6573
	$BaSO_4$	0.2531	9.4033	K_2SO_4	K	2.229	0.3481
Hg_2Cl_2	$SnCl_2$	2.490	0.3962		KCl	1.169	0 0679
$HgCl_2$	Hg_2Cl_2	1.150	0.0607		K_2O	1.850	0.2672
	HgS	1.167	0.0671		K_2PtCl_6	0.3585	9.5545
HgO	Hg_2Cl_2	0.9176	9.9627		SO_3	2.177	0.3379
HgS	$Hg(CN)_2$	0.9210	9.9643		$BaSO_4$	0.7465	9.8731
	$HgNO_3$	0.8860	9.9474	La	La_2O_3	0.8527	9.9308
	$Hg(NO_3)_2$	0.7167	9.8554	Li	$LiCl$	0.1637	9.2140
	HgO	1.115	0.0474		Li_2O	0.4645	9.6670
	HgO	1.074	0.0311		Li_3PO_4	0.1798	9.2548
	$HgSO_4$	0.7843	9.8945		Li_2SO_4	0.1262	9.1012
I	Ag	1.177	0 0706	Li_2O	$LiCl$	0.3524	9.5470
	AgI	0 5406	9.7328		Li_2SO_4	0.2718	9.4342
	KI	0.7645	9.8834		Li_3PO_4	0.3870	9.5877
	Pd	2.379	0.3764	Mg	MgO	0.6032	9.7804
	PdI_2	0.7041	9.8476		$MgSO_4$	0.2020	9.3054
	$Na_2S_2O_3.5H_2O$	0.5113	9.7087		$Mg_2P_2O_7$	0.2185	9.3395
	$AgCl$	0.8855	9.9472		$MgSO_4$	0.2020	9 3054
In	In_2O_3	0 8271	9.9176		$MgNH_4PO_4.H_2O$	0.1565	9.1945
	In_2S_3	0.7047	9.8480		$MgNH_4PO_4.6H_2O$	0.09909	8.9960
Ir	Ir_2O_3	0.8894	9.9491	MgO	$MgSO_4$	0 3349	9.5249
K	KCl	0.5244	9.7197		$Mg_2P_2O_7$	0.3623	9.5590
	K_2O	0.8300	9.9191		$MgCO_3$	0.4782	9.6796
	K_2SO_4	0.4487	9.6520		$MgNH_4PO_4.H_2O$	0.2595	9.4141
	$KClO_3$	0.2822	9.4505		$MgNH_4PO_4.6H_2O$	0.1643	9.2156
	K_2PtCl_6	0.1609	9.2064	Mn	$MnCO_3$	0 4779	9.6793
	Pt	0 4006	9.6027		MnO	0.7744	9.8889
KCl	Ag	0.6911	9 8396		Mn_2O_3	0.6959	9 8426
	$AgCl$	0.5202	9.7162		Mn_3O_4	0.7203	9.8575
	K_2SO_4	0 8557	9.9323		$MnSO_4$	0.3638	9.5608
	$KClO_4$	0.5381	9.7309		$Mn_2P_2O_7$	0.3871	9.5878
	K_2PtCl_6	0.3067	9.4868		MnS	0.6314	9 8003
	Pt	0.7638	9.8830	MnO	$MnCO_3$	0.6172	9.7904
K_2O	KCl	0.6317	9.8005		Mn_3O_4	0 9301	9.9685
	K_2SO_4	0 5405	9.7328		$MnSO_4$	0.4697	9.6719
	$KClO_4$	0.3399	9.5314		MnS	0.8153	9.9113
	K_2PtCl_6	0.1938	9.2873		$Mn_2P_2O_7$	0.4998	9.6988
	Pt	0.4826	9.6536				

CHEMICAL FACTORS — Continued

Sought	Found	Factor	Log	Sought	Found	Factor	Log
o	MoO₃	0.6666	9.8238	NaHCO₃	KHC₄H₄O₆	0 4465	9.6498
	MoS₃	0 4995	9.6985	Na₂O	NaCl	0.5303	9.7245
	MoS₂	0.5994	9.7777		Na₂SO₄	0.4364	9.6399
	PbMoO₄	0.2613	9.4172		Na₂CO₃	0.5849	9.7671
oO₂	MoS₃	0 7492	9.8746		NaHCO₃	0.3690	9 5670
	(NH₄)₂MoO₄	0.7344	9.8659		Na₂HPO₄	0.4365	9 6400
	(NH₄)₂PO₄.12MoO₃	0 9205	9 9640		NaH₂PO₄	0.2583	9.4122
	PbMoO₄	0 3920	9.5931		Na₄H₂P₂O₇	0 2793	9.4461
	HNO₃	0.2223	9 3470		NaHSO₄	0 2979	9.4741
	NO₃	0 3045	9.4835		NaNO₃	0.3647	9.5619
	N₂O₃	0.3686	9.5665		NaOH	0.7748	9 8891
	N₂O₄	0 3045	9.4835		Na₂SO₄	0.4364	9.6399
	N₂O₅	0 2594	9.4140	Na₂SO₃	BaSO₄	0.5401	9.7325
	NaNO₃	0.1618	9 2159	Na₂S₂O₃	BaSO₄	0.3387	9 5298
	NH₃	0.8225	9 9151		Na₂S₂O₃.5H₂O	0.6371	9 8042
	Pt	0.1435	9 1569	Na₂SO₄	BaSO₄	0.6086	9.7843
	NH₄Cl	0.2619	9.4181	Nd	Nd₂O₃	0.8574	9.9332
a	NaCl	0.3934	9 5949	NH₃	HNO₃	0.2703	9.4318
	Na₂SO₄	0.3238	9 5103		H₂SO₄	0.3473	9.5407
	NaBr	0 2235	9 3493		N	1.216	0.0849
	Na₂CO₃	0.4340	9 6375		NaNO₂	0 2466	9.3921
	NaF	0 5476	9 7385		NaNO₂	0 2002	9 3018
	NaHCO₃	0 2738	9 4374				
	NaI	0 1534	9.1858				
	Na₂O	0 7419	9.8704				
	NaOH	0 5750	9 7597				
	Na₄SO₄	0 3238	9.5103				
₂B₄O₇	B₂O₃	1.445	0.1599	NH₄	NH₃	1.059	0.0250
	H₃BO₃	0.8137	9 9105		NH₄Cl	0.3372	9 5279
a₂B₄O₇.10 H₂O	B₂O₃	2.738	0 4375		(NH₄)₂PtCl₆	0.08125	8 9099
	H₃BO₃	1.542	0 1881		Pt	0.1848	9 2668
	KBF₄	0.7573	9.8793	NH₄Cl	AgCl	0.3732	9 5719
aBr	Ag	0.9539	9 9795		NH₃	3.141	0.4971
	AgBr	0.5480	9.7388		(NH₄)₂PtCl₆	0 2410	9.3820
aCl	Ag	0 5418	9 7338		Pt	0.5480	9.7388
	AgCl	0.4078	9 6105	(NH₄)₂SO₄	BaSO₄	0.5661	9.7529
	AgNO₃	0.3441	9.5367	Ni	NiO	0.7858	9.8953
	Na₂O	1.886	0 2756		NiC₈H₁₄N₄O₄	0.2032	9 3079
aF	CaF₂	1.076	0.0317		NiSO₄	0 3792	9.5788
a₂HAsO₃	Mg₂As₂O₇	1.095	0 0392		Ni(NO₃)₂.6H₂O	0 2018	9 3049
	I	0 694	9 8257		Ni₂SO₄.7H₂O	0 2089	9.3200
a₂HAsO₄	Mg₂As₂O₇	1.198	0 0783	NO₂	NO	2 066	0.3152
	I	0 7324	9 8647		NH₃	3.640	0 5612
aHCO₃	CO₂	1.909	0.2808				

Natural Numbers	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
													8	11	14	17	20	22	25
													8	11	13	16	18	21	24
													7	10	12	15	17	20	22
													7	9	12	14	16	19	21
													7	9	11	13	16	18	20
													6	8	11	13	15	17	19
													6	8	10	12	14	16	18
													6	8	10	12	14	15	17
													6	7	9	11	13	15	17
													5	7	9	11	12	14	16
													5	7	9	10	12	14	15
													5	7	8	10	11	13	15
													5	6	8	9	11	13	14
													5	6	8	9	11	12	14
													4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038			4	6	7	8	10	11	12
													4	5	7	8	9	11	12
													4	5	6	8	9	10	12
													4	5	6	8	9	10	11
													4	5	6	7	9	10	11
													4	5	6	7	8	10	11
													3	5	6	7	8	9	10
													3	5	6	7	8	9	10
													3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
													3	4	5	6	7	8	9
													3	4	5	6	7	8	9
													3	4	5	6	7	8	9
													3	4	5	6	7	8	9
													3	4	5	6	7	7	8
													3	4	5	6	6	7	8
													3	4	4	5	6	7	8
													3	4	4	5	6	7	8
													3	3	4	5	6	7	8
													2	3	4	5	6	7	8
													2	3	4	5	6	6	7
													2	3	4	5	6	6	7

Natural Numbers	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS								
											1	2	3	4	5	6	7	8	9
											2	2	3	4	5	5	6	7
											2	2	3	4	5	5	6	7
											2	2	3	4	5	5	6	7
											1	2	3	4	4	5	6	7
											1	2	3	4	4	5	6	7

ANTILOGARITHMS

Logarithms	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS								
											1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	3
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
[illegible]	[illegible]	[illegible]	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	2	2388	2393	1	1	2	2	3	3	4	4	5
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	8	2443	2449	1	1	2	2	3	3	4	4	5
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	95	2500	2506	1	1	2	2	3	3	4	5	5
[illegible]	[illegible]	2518	2523	2529	2535	[illegible]	[illegible]	53	2559	2564	1	1	2	2	3	4	4	5	5
.41	[illegible]	[illegible]	[illegible]	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	42	2748	1	1	2	3	3	4	4	5	6
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	05	2812	1	1	2	3	3	4	4	5	6
[illegible]	[illegible]	[illegible]	2831	2838	2844	[illegible]	[illegible]	[illegible]	71	2877	1	1	2	3	3	4	5	5	5
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	85	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	[illegible]	[illegible]	[illegible]	55	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	26	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

Logarithm	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS								
											1	2	3	4	5	6	7	8	9
													3	4	4	5	6		7
													3	4	5	5	6		7
													3	4	5	5	6		7
													3	4	5	6	6		7
													3	4	5	6	6		7
												2	2	3	4	5	6	7	7
												2	3	3	4	5	6	7	8
												2	3	3	4	5	6	7	8
												2	3	4	4	5	6	7	8
												2	3	4	5	6	7	7	8
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														9	11	12	14	16
														9	11	12	14	16

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